The Topochemical 1,6-Polymerization of a Triene

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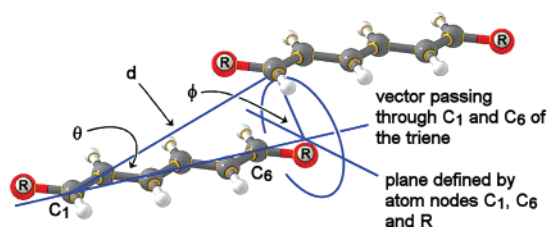
Received June 25, 2002

The control of polymer structure at both the molecular and supramolecular level is an important goal for the preparation of new materials with designed properties. One approach to control polymer structure is to preorganize the monomers in the condensed phase to carry out a topochemical polymerization.[1] Unfortunately, topochemical polymerizations are rare; only a few fundamental types are known. One of the best examples is the topochemical polymerization of diacetylenes.[2] If diacetylenes are properly organized in the condensed phase, then they polymerize to give the corresponding polydiacetylene. The original polydiacetylenes were a fortuitous discovery. Compounds were found that crystallized with the necessary structural parameters. Once these compounds were discovered, certain supramolecular structural features were recognized that led to other examples, some by design and others by serendipity. However, most diacetylenes do not crystallize with the required preoganization, and the corresponding polydiacetylenes are simply unknown.

Dienes have recently been reported to undergo topochemical polymerization.[3] Certain dienes crystallize with the necessary parameters for polymerization; a few principles have been formulated, but there is no general route to topochemical diene polymerizations.[4]

We developed a host−guest strategy for the polymerization of diacetylenes.[5,6] Diacetylene monomers were cocrystallized with a suitable host molecule that imposed the necessary structural parameters upon diacetylene guest molecules. This led to new polydiacetylenes and a partial solution to the general synthetic problem. This strategy also was successful for the more challenging problem of 1,6-triacetylene polymerizations; no serendipitous triacetylene polymerization had ever been found. Using the host−guest strategy we reported the first example of a 1,6-triacetylene polymerization, a topochemical synthesis by design.[7]

The topochemical 1,6-polymerization of a triene is an unknown transformation. In fact, there are few reports of any 1,6-triene polymerization. In addition to the tacticity problems of associated with 1,6-substituted trienes, competition between the 1,2-, 1,4-, and 1,6-polymer reaction pathways is to be anticipated. In principle, preorganizing the reactants in the solid state can suppress these alternate reaction pathways as well as control the stereochemistry of the new stereocenters. For a successful topochemical polymerization, molecular modeling (MM2) suggests the trienes should be translationally spaced with a repeat distance of about 7.2 Å (Figure 1). If the trienes also are aligned with a tilt angle, θ, of about 29°, the reacting carbon atoms (C_1−C_6) of adjacent π-systems will approach each other to within a close contact ($\sim$3.5 Å).

Since these supramolecular structural features are very similar to those we previously used to produce the first triacetylene polymerization,[7] we decided to explore the same strategy for a 1,6-

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Figure 1. The relative orientation and alignment of two trienes related by translational symmetry can be specified by three parameters. The repeat distance **d**, a tilt angle θ, and an orientation angle ϕ.[8] Model calculations suggest that a repeat distance of about 7.2 Å and a tilt angle of about 29° will bring neighboring C_1 and C6 carbon atoms into near van der Waals contact. An orientation angle, ϕ, of 90° would give the maximum $\pi-\pi$ overlap, but observations with diene polymerizations suggest that this angle may vary considerably.
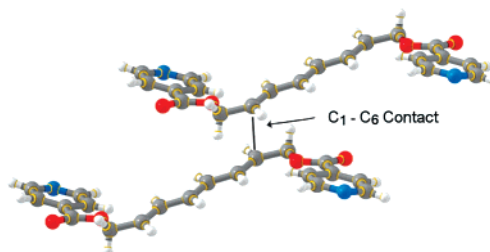
Figure 2. The X-ray crystal structure of **1**. The observed repeat distance is 7.252 Å, the tilt angle θ is 34°, the orientation angle ϕ is 68°, and a C_1-to-C_6 contact is 4.09 Å.

triene polymerization. This approach involves the use of two molecules; one acts as the host, controlling the supramolecular structure and establishing the 7.2 Å translational repeat distance, and the other, the guest, is the intended triene monomer. The host would be a carboxylic acid, and the guest, a dipyridine or vice versa.

Several different host and guest molecules have been synthesized, and a search for suitable host−guest crystals is underway. However, in pursuit of this strategy serendipity has paid us a call.
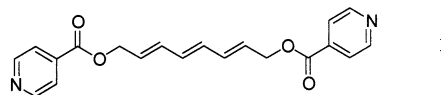
One of our intended triene guest molecules, **1**, was prepared in a five-step sequence from diethyl fumarate.[9,10,11] The crystal structure of **1** was determined and is shown in Figure 2.

We observed that adjacent triene molecules have a supramolecular structure that might be suitable for a topochemical polymerization. Although the 1−6 carbon−carbon atom distance (4.09 Å) of adjacent trienes is a little long based on data from topochemical diene and diyne polymerizations, we nevertheless decided to explore the thermally induced polymerization of triene, **1**.
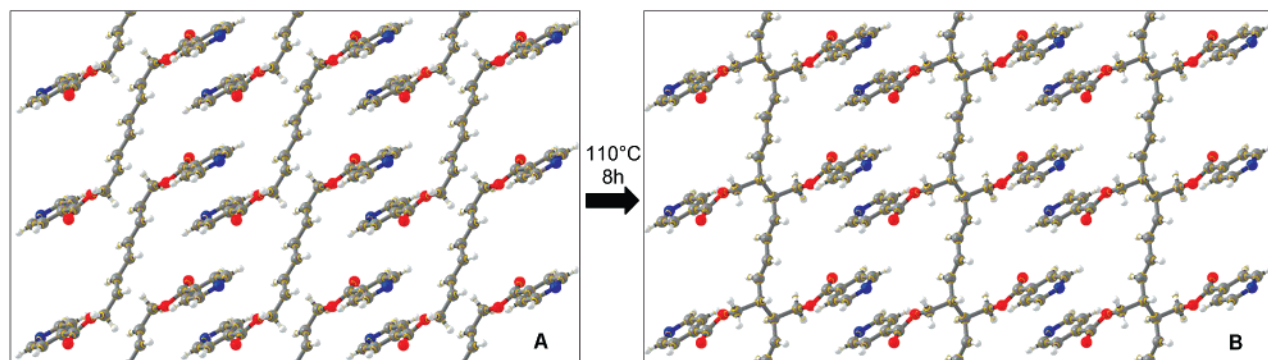
Figure 3. (a) Crystal structure of **1**. Upon heating at 110 °C for 8 h the molecules undergo a topochemical polymerization. (b) Crystal structure of the *meso*-diisotactic polymer. Both structures were determined by an X-ray study of the same single crystal.

The single crystal that produced the structure shown in Figures 2 and 3A was heated to 110 °C for 8 h.[12] This process resulted in a smooth transformation to a new material whose X-ray crystal structure determination (Figure 3B) clearly demonstrated that a topochemical 1,6-polymerization of the triene to a polytriene had occurred.

Is the packing of triene, **1**, with the correct supramolecular structural parameters for a topochemical polymerization, a chance observation, or is there some unexpected supramolecular feature that might lead to additional examples? Inspection of the crystal structure of triene, **1**, illustrates that $\pi-\pi$ stacking of the pyridine rings plays a role determining the supramolecular structure of this compound. This is a common structural motif for aromatic rings, particularly pyridine derivatives.[13] On the basis of a crystal structure analysis of pyridine derivatives in the Cambridge Structural Database (CSD) a model for $\pi-\pi$ stacking was developed.[13] Adjacent pyridine rings are staggered with the local dipoles of the pyridine rings pointing in opposite directions, presumably to minimize electrostatic repulsions. The plane−plane distance between adjacent rings in a dimer is commonly around 3.57 Å. Further for $\pi-\pi$ stacking of these dimers leads naturally to a translational repeat distance of about 7.2 Å between the first and third symmetry-equivalent molecules. A search of the CSD for crystal structures of simple isonicotinate derivatives resulted in only isonicotinic acid and an ester derivative.[14] The pyridine rings of both of these structures pack according to the reported model for $\pi-\pi$ stacking. The translational distance between first and third pyridine rings was 7.23 Å for isonicotinic acid and 7.28 Å for the diester derivative. Thus, the packing of the pyridine rings of the triene **1** is in accord with the reported model and limited data on analogous isonicotinate derivatives.

However, the organization of trienes with 7.2 Å repeat distance is, by itself, not a sufficient supramolecular structural feature for the topochemical 1,6-polymerization. In addition, C_1 and C_6 atoms of adjacent triene chains must have a close contact, preferably under 4 Å.[15] If the translational repeat distance of the chains is 7.2 Å and the triene chains pack with a spacing of 3.5 Å, then the C_1 and C_6 atoms will come into close contact (see Figure 1). It is reasonable to conclude that there is a good probability of successfully organizing trienes for a topochemical 1,6-polymerization using $\pi-\pi$ stacking.

Although the polymerization of triene **1** was a serendipitous discovery, it clearly demonstrates that the topochemical polymerization of a triene is possible, thus adding it to the small but growing number of important topochemical reactions. Because this reaction produced a single crystal of the polymer, it represents an unequivocal example of a polytriene whose molecular and supramolecular structure are precisely known.

Supporting Information Available: X-ray and synthetic data for compound **1** and its polymer (PDF/CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) The monomer **1** ($C_{20}H_{18}N_2O_4$) crystallizes in the space group $P2_1/c$ with $a = 9.912(4)$ Å, $b = 7.252(3)$ Å, $c = 13.582(4)$ Å, $\beta = 114.3(5)°$, $V = 889.6(5)$ Å^3, $Z = 2$. The crystals were of poor quality, and even the best crystal gave only a limited number of data on a Bruker Smart CCD diffractometer. $R = 0.071$, $R_w = 0052$ (357 reflections with $I > 3.00\sigma(I)$, 118 variables). After a heat treatment of 110° for 8 h, the identical crystal was returned to the diffractometer, and the structure of the polymer of crystal **1** was obtained. Space group $P2_1/c$ with $a = 11.183(4)$ Å, $b = 7.204(3)$ Å, $c = 11.683(4)$ Å, $\beta = 118.9(5)°$, $V = 860.6(5)$ Å^3, $Z = 2$, $R = 0.087$, $R_w = 0048$ (333 reflections with $I > 2.00\sigma(I)$, 98 variables). The polymerization experiment was confirmed by studies on additional single crystals, which gave similar crystallographic results.
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JA027444A