Approaches to Conjugated Polymers *via* New Solid State Polymerizations

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Summary: Solid state polymerization is the most convenient approach for the synthesis of macroscopic polymer single crystals. Motivations for seeking fully crystalline specimens of conjugated polymers other than polydiacetylenes (PDA) are presented. The thermal reactivity of *p*-ethynylbenzoiic acid (EBA) is found to be a topochemically initiated solid state polymerization. The studies of EBA led to a new paradigm for solid state reactivity in such systems. Systems related to the paradigm, namely *p*-cyanobenzoic acid (CNBA) and *p*-cyanocinnamic acid (CNCA) have been studied. Sublimation competed with thermal processes in CNBA and CNCA, and a detailed product description has proved difficult to date. Thermochromism and charge-transfer transitions in PDA are discussed.

Keywords: conjugated polymers; monoacetylenes; nitriles; polydiacetylenes; solid state polymerization; thermal reactivity

Introduction

The 2000 Nobel Prize in Chemistry [1-3] awarded to H. Shirakawa, A.G. MacDiarmid, and A.J. Heeger, is a clear recognition of the impact that conjugated polymers have had in the areas of scientific, technological, and commercial activity. Yet, when placed in a broader context of materials, as will be done herein, it is apparent that there is considerable opportunity for further progress in this area of endeavor.

Many classes of materials, but especially inorganic semiconductors, exist in both crystalline and amorphous forms. The disordered structure of the amorphous forms leads to lower carrier mobilities, and the electrical properties of amorphous forms are inferior to those of single crystals.[4] Crystalline silicon is an indirect band gap semiconductor while its amorphous form has a direct gap. The temperature dependence of the conductivity of the two forms is significantly different at low temperatures.[5] Nevertheless, amorphous semiconductors are readily fabricated into large area thin film devices with commercially viable applications such as those known for the amorphous chalcogenides Se and As_2Se_3. The latter have been

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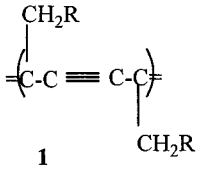
extensively used in copying machines as photoreceptors.

The majority of the research and successes to date in the area of conjugated polymers have been largely achieved in materials that are amorphous or partially crystalline at best.[1-3] While the need for improved structural order has been emphasized,[3] the existing materials, with the single exception of polydiacetylenes (PDA), are amorphous materials whose fully crystalline analogs are unknown materials whose properties can occasionally be guessed at, for example, by extrapolation of the properties of rigorously defined oligomers.[6] The molecular structures of the PDA under discussion are given in Figure 1. That we are missing substantial information with the lack of numerous fully crystalline conjugated polymers can readily be grasped from the example of the electronic spectrum of a PDA that has both crystalline and amorphous forms, namely PDA-4-BCMU.[7] (Scheme 1, **1a**) With light polarized parallel to the conjugated polymer chain, the crystalline form exhibits an intense spectral maximum at 633 nm with vibronic structure. Perpendicular to the conjugated chain, the spectrum is markedly weaker and featureless, as expected for an anisotropic material. In contrast, the amorphous film exhibits broad maxima at 526 and 488 nm. Clearly, there is markedly less information in the spectrum of the amorphous PDA film relative to that of the single crystal polymer specimen. By extension, there is considerable loss of information in the spectral and other properties of the large number of reported amorphous conjugated polymers.

PDA are a class of fully crystalline conjugated polymers whose modern study was pioneered by G. Wegner and coworkers. By far, PDA constitute the best-known class of fully crystalline conjugated polymers.[8-15] As a consequence of their synthesis by topochemical (atoms making a new covalent bond are separated by about 3.8-4.2Å in the reactant crystal structure) and topotactic solid state polymerization, many PDA are available in the form of macroscopic single crystals, and hence provide several examples of the best defined polymers.[8-15] As such, PDA join the metallic and superconducting sulfur nitride[16] and dihalobis (*tris* 2-cyanoethylphosphine) nickel (II) polymers[17] as examples of crystallographically defined polymers obtained via solid-state polymerization.[10] The diacetylene (DA) polymerization process is more general than the other cases.

While PDA clearly have attractive physical properties, there are good scientific and technological reasons for seeking other examples of fully crystalline conjugated polymers. If one is interested in polymers that exhibit fluorescence and properties related to fluorescence such as electroluminescence, crystalline PDA have very low quantum yields of fluorescence,[13] and other examples must be sought. In addition, approaches to fully

crystalline conjugated polymers other than PDA will involve the development of new organic solid-state reactions that will be driven by finding new examples of supramolecular crystal chemistry and elucidation of the role of the crystal chemistry in chain initiation and propagation.



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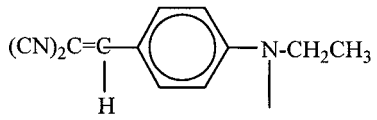
a. R = -$(CH_2)_3$-OC(O)-NH-CH_2-C(O)-OnC_4H_9, 4-BCMU

b. R = -$(CH_2)_3$-OC(O)-NH-CH_2CH_3, ETCD



Scheme 1. Polydiacetylene repeat unit and the structures of side groups under discussion.

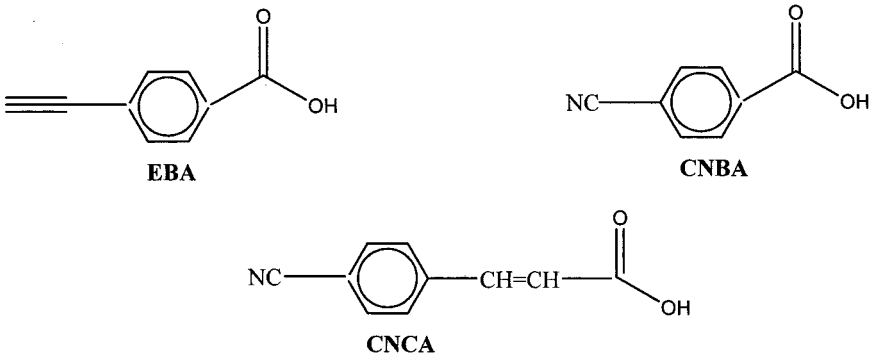
In this paper, we revisit earlier interest[18,19] in monoacetylene reactivity via study of the thermal reactivity of *p*-ethynylbenzoic acid (EBA). Through our studies of EBA reactivity, we developed a new paradigm for the study of solid state reactivity of various acetylenic derivatives and nitriles. We find that two common aromatic nitriles are not particularly reactive in the solid. Finally, we summarize recent developments in PDA research.

Thermal Reactivity of *p*-Ethynylbenzoic Acid

It was reported that *p*-ethynylbenzoic acid (EBA, Scheme 2) exhibited undefined solid-state reactivity.[20] Indeed, it had been proposed[21] that EBA underwent a slow solid-state polymerization at room temperature, and it was noted[21] that the sodium and potassium salts of EBA were stable. While it is apparent from earlier literature[20,21] that EBA is reactive in the crystalline state, the crystallographic basis of the reactivity was unknown as was the structure and nature of the product.

p-EBA is a monoclinic crystal, space group $P2_1/n$, a = 3.8684 Å, b = 6.2329 Å, c = 30.1900 Å, β = 90.281°, V = 727.90 $Å^3$. The a-axis dimension clearly indicates a linear chain structure, and there are short crystallographic contacts between acetylenic carbons in the same chain (3.711 Å) and 3.828 Å between chains. While there is a linear chain structure it is not interdigitated. Such a situation was proposed[22] from X-ray powder data and molecular modeling for esters of EBA. The hydrogen-bonding pattern of the carboxyl group is the

common one. These crystallographic contacts form the structural basis for the reactivity that is observed. The interchain contacts are further examples of acetylenic C-H-π interactions.[23,24] The EBA crystal was not sensitive to uv light and X-rays, and exposure to 50 Mrad of ^{60}Co γ-radiation did not lead to detectable reaction.



Scheme 2. Molecular structures of monomers under discussion.

The discussion now turns to the structure and properties of the product of the thermal solid-state reaction of EBA, which is red in color and amorphous by X-ray powder diffraction. The exotherm from diffeential scanning calorimetry at a heating rate of 10°C/min. is shown in Figure 1, along with the second scan. The lack of features in the second scan indicates that the polymerization was completed during the first scan. In view of the crystal structure of EBA, it is conceivable that the product of a thermal solid-state reaction could involve a Strauss dimerization[25], a cyclotrimerization[26] as in an acetylene-terminated oligomer, and also a solid-state polymerization to a polyphenylacetylene derivative. Since the product of cyclotrimerization of EBA is a colorless crystal[27] , this process is not involved in the thermal solid-state reaction of EBA. By comparison of the ^{1}H NMR, uv-visible, and fluorescence spectra of the thermal product of EBA to those of polyphenylacetylene (PPA), it was concluded that the product of thermal reaction of EBA is a substituted-PPA.[28] The N,N-dimethylformamide solution fluorescence spectrum of poly-EBA exhibits a maximum at 461 nm with 400 nm as excitation wavelength. In a subsequent thermal process, the polyphenylacetylene derivative is converted to the known[27] cyclotrimer. The analogous process is known for PPA.[29]

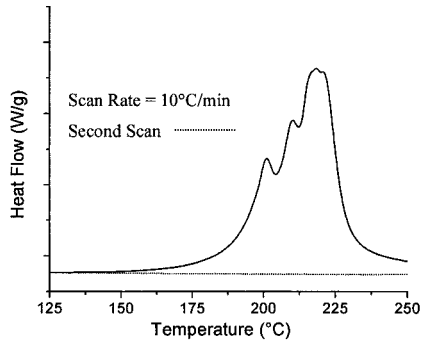


Figure 1. Differential scanning calorimetry of the thermal polymerization of EBA.

A Paradigm for Solid State Reactivity of Aromatic Acetylenes and Nitriles

In the interest of identifying a large family of structures to investigate solid-state reactivity that could, in principle, lead to fully crystalline conjugated polymers, we note that *p*-cyanobenzoic acid (CNBA, Scheme 2) is isoelectronic to EBA. It is useful to note that the molecular structures of EBA and CNBA belong to a family represented by the general formula given in Figure 2.

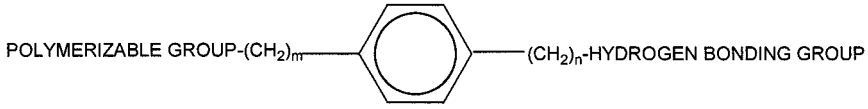


Figure 2. General molecular formula for solid state reactive compounds.

For the formula in Figure 2, the polymerizable groups would be alkyne, haloalkyne, propyne, and nitrile. The product of nitrile polymerization would be a polyimine. The most commonly used hydrogen bonding groups would be carboxyl and amide. In Figure 2, for EBA and CNBA, m=n=0. The perspective of Figure 2 clearly outlines considerable work for the future.

Reactivity of *p*-Cyanobenzoic Acid and *p*-Cyanocinnamic Acid

Given the observed thermal reactivity of EBA, we deemed it of interest to inquire into the behavior of the isoelectronic CNBA. Indeed, the Aldrich catalog[30] tells the reader that CNBA melts with decomposition. Yet, it has been reported[31] that CNBA exhbiits a melting point.

However, recording of a melting pont in a capillary tube, at first glance, indicates a reversible melt. The issue was resolved by differential scanning calorimetry. Figure 3 shows the first and second scans for heating of CNBA. Clearly a decomposition is involved.

We have observed that heating of CNBA at 150°C converts the colorless crystals to a yellow solid, but the yellow color is due to a very small amount of product. Prolonged heating leads to a black solid in a yield that is 1% at most. Figure 4 shows the FTIR spectrum of this material. It lacks the absorption due to cyano stretching found in the spectrum of CNBA. Like EBA, CNBA has a linear chain crystal structure[32] with a stacking axis dimension of 3.831 Å, but it is not isomorphous to the EBA structure. We assume that the thermal reaction of CNBA involves intermolecular reaction involving the cyano groups, as suggested by the crystal structure. No significant reactivity was detected after we exposed CNBA to 50 Mrad ^{60}Co γ-radiation.

The thermal reactivity of *p*-cyanocinnamic acid (CNCA, Scheme 2) is also of interest. It has been reported[33] that CNCA turns red near its melting point. It also has a linear chain crystal structure[34] and exhibits normal cinnamic acid 2+2 cycloaddition. We verify that the red material does form, and we have attempted to isolate significant quantities of the red material by prolonged heating of CNCA near its melting point. Detailed definition of the red material has not been straightforward, as CNCA sublimes faster than it reacts.

Thermochromism in Urethane-substituted Polydiacetylenes

The PDA of the *bis*-alkylurethanes of 5,7-dodecadiyn-1,12-diol exhibit thermochromism. The electronic spectrum of PDA-ETCD (**1b**) shifts from a maximum at 635 nm at ambient temperature to 540 nm above 130°C.[35] The structural changes associated with thermochrmism in these materials have long been of interest. These changes involve a first order phase transition with an expansion of the volume of the unit cell.[36] We have been able to associate the thermochromic transition with mechanical strains on the PDA backbone through ^{13}C CPMAS NMR studies[37], especially involving a nonthermochromic form of **1b** where the mechanical strains have been removed by boiling with chlorobenzene. A further assessment of the details of such mechanical strains will require good crystallograpic data. Since the crystals of **1b** are disordered, [38] a direct appraoch has not proved satisfactory. The structure of the ETCD monomer[39] has been solved, and it reveals intermolecular distances that are near optimal[8] for reactivity. Further study of the structure as it converts to polymer is necessary.

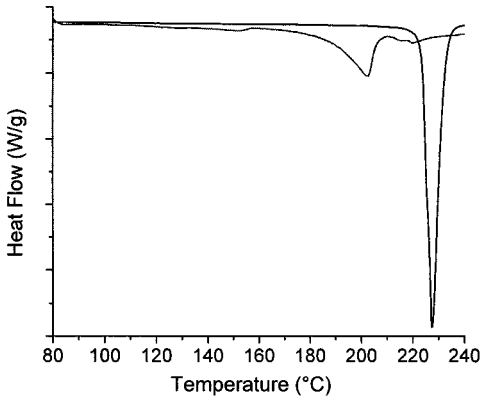


Figure 3. Melting behavior of CNBA by differential scanning calorimetry. The first scan has an endotherm of 220.0 J/gm. While the heat associated with the second scan is 62.6 J/gm.

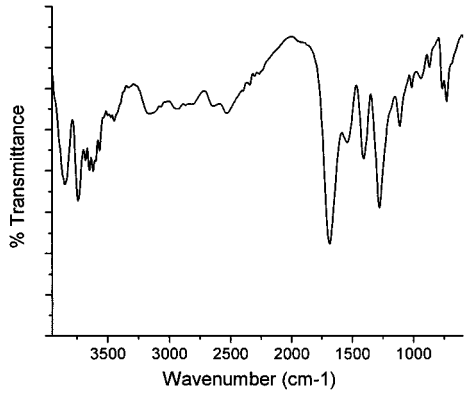


Figure 4. FTIR spectrum of the product of thermal reaction of CNBA.

Polydiacetylene Spectral Features Below the Exciton

The PDA of 1,6-diethyl-(1,6-bis-*p*-benzylidenemalononitrile)-2,4-hexaidyndiamine (**1c**) in single crystal form exhibits[40] heretofore unobserved spectral features in both principal directions from about 833-625 nm. The energy of this band, its width, lack of vibronic structure, and apparent polarization suggest that it arises from one or more charge-transfer transitions. The donor would be the conjugated backbone, and the acceptor would be a side group of an adjacent chain. Subsequently, such absorption was reported[41] in another PDA.

Acknowledgements

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