

Semiempirical study of low molecular weight polymers of 3-phenyl-1-ureidonitrile

Ari Silver, Hua Dong, Zhengfei Sun, Karl Sohlberg*

Department of Chemistry, Drexel University, Philadelphia, PA 19104, USA

Received 17 May 2005; accepted 23 June 2005

Available online 25 August 2005

Abstract

Conformational searching and semiempirical (AM1) structure optimizations have been carried out on low degree polymers of 3-phenyl-1-ureidonitrile (PUN), a system of interest for its potential application in thin-film ultra-high-density data storage. The predicted structural properties and vibrational frequencies are in good agreement with experimental data. Most notably, a downshift in this C–N stretching frequency upon polymerization and the absence of a peak near 2200 cm^{-1} in both the experimental and theoretical IR spectra, support the proposal that PUN film polymerizes by opening of the C≡N bond.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Semiempirical calculations; Organic substances; Thin films; Information storage

1. Introduction

In recent years, there has been considerable interest in the possibility of achieving ultra-high-density data storage by manipulating matter at the nanometer scale. An important advance in this area has been reported by Ma et al. [1–7] who have demonstrated nanometer scale conductance transitions in various thin organic films. In their experiment, a film is formed by vapor deposition on a highly ordered pyrolytic graphite (HOPG) support. The conductivity of nanometer diameter ‘spots’ of the organic film is seen to increase by several orders of magnitude upon exposure to a brief voltage pulse applied perpendicular to the film, typically using a scanning tunneling microscope (STM) tip [8,9]. Closely spaced sub-nanometer-diameter spots have been achieved, demonstrating that bit densities near 10^4 per square centimeter are theoretically possible [3,4,6]. One thin-film material that has been used successfully in this demonstration is 3-phenyl-1-ureidonitrile (PUN) [3]. It is observed that the vapor deposition produces a thin-film

of crystalline molecular PUN. It is proposed that upon exposure to the brief voltage pulse the film polymerizes locally by opening of the nitrile bond, resulting in a higher conductivity material in the polymerized region. The polymeric form is characterized by a downward shift in the wavelength of the IR adsorption peak assigned to the C–N stretching band and an average molecular weight of 1300, which corresponds to an average degree of polymerization of $n=8$ [6,10].

In this paper, we present a theoretical study of low molecular weight polymers of PUN. Models of PUN with polymerization of degree $n=1-8$ were constructed following the polymerization mechanism described by Ma et al. [3]. The monomer, dimer, and trimer structures are shown schematically in Fig. 1. The computational challenge presented by the large molecular size (particularly at higher degrees of polymerization) is met with a two-fold approach: first, computationally efficient semiempirical methodology is used to model the electronic structure. Second, to accelerate conformational searching we leverage the polymeric nature of the system by computationally mimicking the mechanism of synthesis. The theoretical calculations predict physical observables for the monomer and polymeric species that are in very good agreement with experiments and therefore support the proposed mechanism of polymerization.

* Corresponding author. Tel.: +1 215 895 2653; fax: +1 215 895 1265.
E-mail address: sohlbergk@drexel.edu (K. Sohlberg).

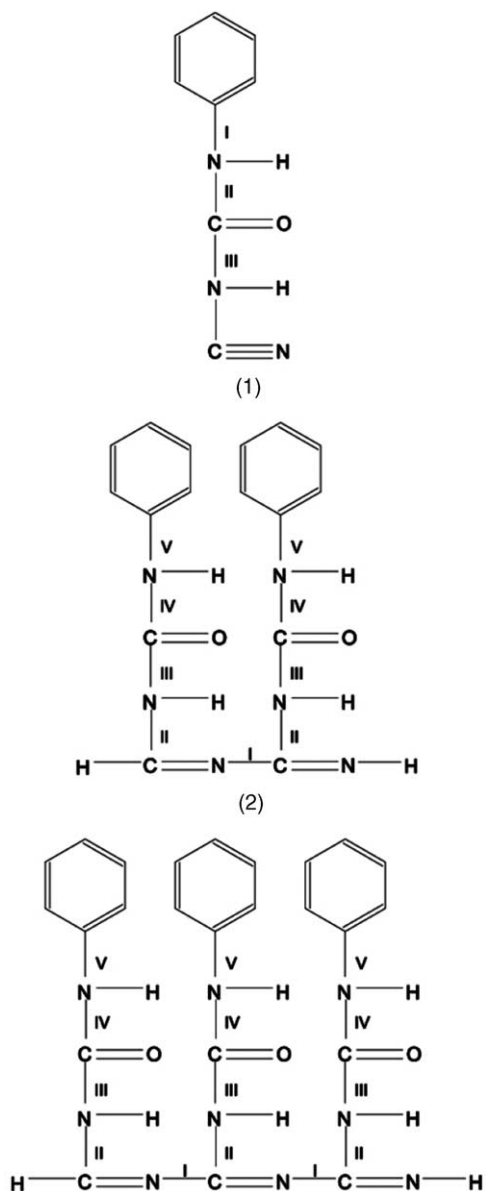


Fig. 1. The PUN monomer (1), dimer (2) and trimer (3). The roman numerals denote key torsion angles.

2. Computational methods

Low-energy structures for the monomer and low-molecular-weight polymers of PUN were identified by conformational searching (as described in Sections 2.1–2.3). An exhaustive conformational search was conducted on the monomer (1-mer), a quasi-exhaustive (QE) search was conducted on the dimer (2-mer) and synthesis mimicking searching (SMS) was performed on the trimer (3-mer) through the octamer (8-mer) [excepting the heptamer (7-mer) for reasons detailed later]. All structural optimizations were carried out with the semiempirical AM1 method [11] as coded in the GAMESS package [12]. The AM1 method was used because the systems chosen lie within the scope of applicability of the AM1 method, which is a widely

accepted and generally reliable semiempirical method. Additionally, in this work, direct comparison is made to experimental vibrational frequencies and AM1 arguably provides more reliable frequency information than any other method that is computationally feasible for the PUN octamer given the available computing resources. Ab initio methods were considered and deemed too computationally intensive to allow the conformational searches to be conducted within a reasonable period of time. Molecular mechanics methods would be dramatically more computationally efficient, but changes in the atom types at each polymerization step would complicate the direct comparison of structures at different degrees of polymerization.

The conformational searching was carried out using a series of domestically developed codes to generate the trial structures and monitor the results of the subsequent optimizations. These codes were implemented as a series of Perl subroutines. Perl was chosen because it is a mature language that couples the flexibility of scripting languages with the power of C. It also has built-in text-processing capabilities, a feature valuable when extracting data from output files. A number of auxiliary subroutines that encapsulated interactions with GAMESS, e.g. the creation of input files and the processing of log files, were also written.

2.1. Monomer exhaustive search

The PUN monomer was subject to an exhaustive search over the three dihedral angles denoted I, II, and III in Fig. 1. These three dihedral angles encompass the three single bonds in the molecule about which there is relatively free rotation. The dihedral angles were all rotated in 60° increments, from -180° to 180° , yielding a total of six trial structures per angle. Taken together, the three dihedral angles provide 6^3 , or 216 trial structures to optimize. The algorithm followed for this conformational search is described in Appendix A.

The exhaustive search yielded two stable conformers of the PUN monomer. A normal mode vibrational analysis on the optimized molecules found $3N-6=51$ positive, real vibrational frequencies, confirming that local minima in the potential energy surface had been located (the PUN monomer contains $N=19$ atoms).

2.2. Dimer quasi-exhaustive search

The PUN dimer (see Fig. 1) was constructed from two monomer units assuming the polymerization mechanism proposed by Ma. et al. [3]. In this mechanism, the $C\equiv N$ (nitrile) bond of the first monomer is changed to a double bond to facilitate bonding to the second monomer unit.

An exhaustive conformational search on the dimer would be computationally infeasible. There are a minimum of nine dihedral angles to iterate over, which would yield a total of 6^9 , or 10,077,696 trial structures (using a 60° resolution).

Download English Version:

<https://daneshyari.com/en/article/9590565>

Download Persian Version:

<https://daneshyari.com/article/9590565>

[Daneshyari.com](https://daneshyari.com)