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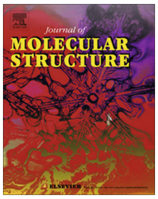

Synthesis and spectroscopic characterization of a new (aryl-SCN)$_n$ polymer: Polythiocyanatohydroquinone

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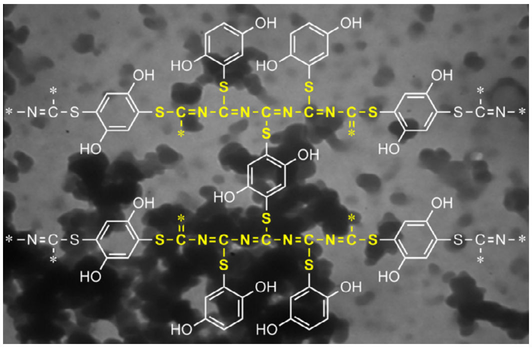
HIGHLIGHTS

- The branched polymer was synthesized from the 1,4-benzoquinone and NH_4SCN reagents.
- The polymer represents (aryl-SCN)$_n$ compound named polythiocyanatohydroquinone.
- DFT calculations confirm the linear chain structure of polymer.
- XRD pattern analysis indicates the amorphous structure of the synthesized polymer.
- This new material stabilizes the colloidal solutions of Ag and Au nanoparticles.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present work we have demonstrated the first synthesis of the polythiocyanogen-like (aryl-SCN)$_n$ compound (polythiocyanatohydroquinone) from the initial 1,4-benzoquinone and NH_4SCN reagents under the normal conditions in the glacial acetic acid medium. The synthesized amorphous polymer was characterized experimentally by the FT-IR and UV–vis spectroscopic methods accompanied with theoretical assignments by the density functional theory (DFT) and time-dependent DFT calculations. The transmission electron microscopy and the XRD pattern analysis were used to indicate the amorphous structure of the synthesized polymer. The DFT geometry optimization of a number of oligomers ($n = 4$–8) permit us to predict the possible structure of polythiocyanatohydroquinone and to assign the observed bands in IR and UV–vis absorption spectra.

It was found that the synthesized polythiocyanatohydroquinone powder has a complicated structure which can be represented as a branched polymer constructed from the mono- and doubly-SCN-substituted benzene-1,4-diol moieties. This new material demonstrates a good stabilizing effect in respect to colloidal solutions of Ag and Au nanoparticles. Additionally, polythiocyanatohydroquinone is predicted to be a promising candidate for creation of metal-containing composite materials. Its application as a framework for the Pt electrode closing is found very useful.

Introduction

During last decades the organic polymers attract the growing interest because of their wide applications in molecular electronics and power sources technologies [1–9]. Such polymers can be applied as the charged-carriers transfer layers in organic

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light-emitting diodes (OLEDs), in plastic solar cells, or as photo- and electroluminescence generation materials in various power-conversion devices [1–4]. It is especially valuable if the one and the same monomer has a tendency toward production of polymers which differ in a number of the growth dimensions (i.e. 1D linear chains, 2D frameworks and 3D superstructures) [5–7]. For example, the tetraphenylporphyrin, phthalocyanine and tetraoxa [8] circulene can form the linear 1D and reticular 2D polymers greatly differ in their semiconducting properties [5,8–10]. There are many other examples of such bifunctional monomers [5] and one of them is the inorganic thiocyanogen monomer $(SCN)_2$ [11] which can be obtained by oxidation of the SCN^- anion. Free thiocyanogen is an unstable compound which polymerizes quickly producing the insoluble polythiocyanogen $(SCN)_n$ [11]. This polymer is known for a long time and some ways for its practical utilization were proposed including the photocatalytic applications [12–14] and photovoltaic [15–17] devices. However, there is no consensus in the literature concerning the structure of the $(SCN)_n$ polymer. The most reliable structure of $(SCN)_x$ in the form of 1,2,4-dithiazole rings linked by nitrogen bridges (Fig. 1a) was proposed recently by Woollins and coauthors [18] on the ground of the NMR, IR, and Raman spectral data of high quality which were accompanied by the MALDI TOF mass-spectroscopic data. From the other hand, Cataldo et al. have proposed the rather different $(SCN)_x$ structures in the form of linear unbranched $-(S-C{=}N)_x-$ chains [19] or in the form of $-(C{=}N)_x-$ chains cross-linked by the disulfide —S—S— bridges between the Carbon atoms (Fig. 1b) [20,21]. However, as was mentioned in Ref. [18] the Cataldo's structures are less probable and have not been proved sufficiently well by spectroscopic data in a contrast to the structure of Woollins (Fig. 1a).

At the same time, we should stress that the S-closed thiocyanates, like the (thiocyanatomethyl)benzene and similar species [22,23], would provide predominantly the linear polymerization upon the corresponding conditions. In the present work we have described the first synthesis and spectroscopic IR and UV–vis characterization of the polythiocyanatohydroquinone (hereinafter PTHQ) (Fig. 1c) together with the DFT assignment of the observed FT-IR and UV–vis spectra.

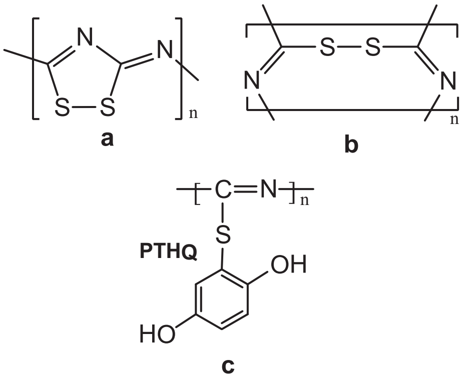


Fig. 1. The different structures of polythiocyanogen $(SCN)_n$ and the proposed structure of synthesized polythiocyanatohydroquinone (PTHQ).

Experimental section

The target PTHQ compound was synthesized by the three-stage synthesis presented in Scheme 1. The 1,4-benzoquinone crystal was dissolved in the glacial acetic acid (GAA) and treated with the NH_4SCN salt in the GGA medium. The forming benzene-1,4-diol and thiocyanogen at the same conditions produce next the *ortho*-substituted 2-thiocyanatobenzene-1,4-diol which polymerizes rapidly into the target PTHQ compound. The orange-brown PTHQ polymer was precipitated by water, filtered, washed and dried upon the 80 °C.

The IR spectrum of prepared PTHQ was measured with the PerkinElmer Spectrum One FT-IR Spectrometer in a KBr pellet. The UV–vis spectrum of the PTHQ has been carried out on a SF-26 spectrophotometer in a DMSO solution with the PTHQ concentration 20 mg dm^{-3}. The transmission electron microscopy (TEM) experiment was carried out using the SELMI TEM 125 K microscope. The XRD pattern analysis was performed by the DRON-3 X-ray diffractometer.

Calculation details

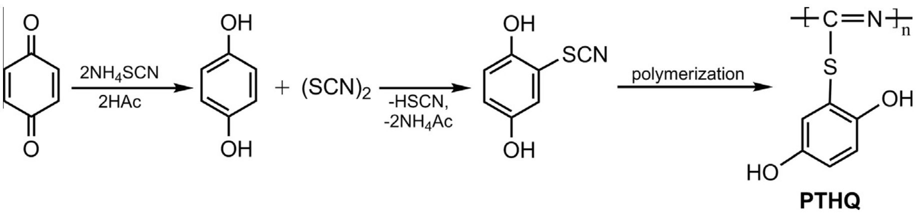
The structures of the studied PTHQ oligomeric models (n = 4–8, Scheme 1) were optimized by the density functional theory (DFT) method using the B3LYP hybrid functional [24,25] with the 6-31G(d) basis set [26]. We have also calculated the force fields and IR absorption spectra of the proposed PTHQ models (n = 4–8). All vibrational wavenumbers were found to be real which indicates the finding of the true minimum on the hypersurface of the total energy of the PTHQ oligomers. In order to compare the calculated IR spectra with the experimental FT-IR data much correctly we have employed the scaling factor equal to 0.980 for the calculated vibrational frequencies in the region 1800–400 cm^{-1}.

The electronic absorption spectra of the studied PTHQ oligomers (n = 4–8) have been calculated by the time-dependent (TD) DFT method [27] with the same B3LYP/6-31G(d) approach using also the polarizable continuum model (PCM) [28] to take into account the solvent effect. We have used the DMSO solvent for the PCM model as well as for the experimental measurements of UV–vis spectrum. The calculated electronic absorption spectra of the PTHQ oligomers were created by using the SWizard software [29] (band half-width 2850 cm^{-1}, Gaussian distribution function). All DFT and TD DTF calculations are performed at the PDC supercomputer of the Royal Institute of Technology (Stockholm) with the usage of the Gaussian09 [30] program package.

Results and discussion

IR spectra of PTHQ

In order to explain the possible structure of the PTHQ compound we have provided the detailed band assignment of the



Scheme 1. The three-stage synthesis of polythiocyanatohydroquinone (PTHQ).