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Ultraviolet Photoelectron Spectroscopy Study of the Polydiacetylene of the Bis-*p*-Chlorocinnamate of 10,12-Docosadiyn-1,22-diol and Related Subjects

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The *bis-p*-chlorocinnamate of 10,12-docosadiyn-1,22-diol (Cl-Cin-22) interacts with ⁶⁰Co γ radiation to give a polydiacetylene (PDA) soluble in organic solvents. This PDA has been previously studied with respect to its optical spectroscopy and exciton binding energy. In this work, solution cast films of PDA-Cl-Cin-22 have been studied by ultraviolet photoelectron spectroscopy (UPS). The threshold solid state ionization energy of 5.9 eV is consistent with earlier UPS studies of PDA. Exposure of a Cl-Cin-22 monomer film to He I (21.2 eV radiation) initially gives a blue colored film that converts to a red film on heating, consistent with an irreversible thermochromic transition. *In situ* polymerization in ultrahigh vacuum of spin coated films of Cl-Cin-22 using He I (21.2 eV radiation) has been explored by recording UPS spectra as a function of exposure time, and for comparison UPS data of *p*-chlorocinnamic acid and bis-*p*-chlorotruxinic acid are also reported.

Keywords: Polydiacetylene, ultraviolet photoelectron spectroscopy, ionization energy, thermochromic transition

1 Introduction

Ultraviolet photoelectron spectroscopy (UPS) has been used extensively in the study of the valence band structure of conjugated polymers, including polydiacetylenes (1, 2). We have previously used UPS to study the thermochromic phase transition in polydiacetylenes (PDAs) (3). With the notable exception of PDA, the electrical and optical properties of conjugated polymers are studied on amorphous or partially crystalline specimens. Hence, a discussion of the properties of PDA that are available in both crystalline and amorphous forms is of interest. The optical properties of PDA-4-BCMU have been studied (4) in both crystalline and solvent cast films. The spectra of the solution cast films appear at higher energy and with a loss of vibrational structure compared to the spectrum obtained from crystals. The PDA of the *bis-p*-chlorocinnamate of 10,12-docosadiyn-1,22-diol (PDA-Cl-Cin-22) is also available in crystalline forms, and the crystals are soluble in solvents such as chloroform or chlorobenzene (5–7).

In this paper, we report UPS studies of thin films of PDA-Cl-Cin-22. *In situ* polymerization of Cl-Cin-22 has also been investigated using UV-Vis and UPS.

2 Experimental

Cl-Cin-22 was synthesized and polymerized as previously described (5, 7) with ⁶⁰Co gamma radiation with 50 MRad for 64 h to give a soluble polydiacetylene (PDA) (Fig. 1). Samples for UPS measurements were prepared by spin-coating (2000 rpm) chloroform solutions of Cl-Cin-22 and ⁶⁰Co radiation-formed polymer (6 mM) onto gold-coated silicon wafers. These samples were kept in an electric drier for 24 h to remove residual solvent. Film thickness is critical, as it was found that if the film was not homogeneous and thick enough to cover the entire gold substrate, then gold photoemission signal from the substrate was observed during UPS analysis. In contrast, if the film was too thick, charging due to positive charge buildup on the surface could occur. The prepared samples had thicknesses in the range of 180–240 Å, as measured with a DEKTAK profilometer. Cl-Cin-22 monomer is very sensitive to light, so care was taken to avoid exposure to ambient light before and during UPS and UV-Vis measurements.

UPS measurements were performed in a Vacuum Generators ESCALAB MKII instrument with a base pressure of

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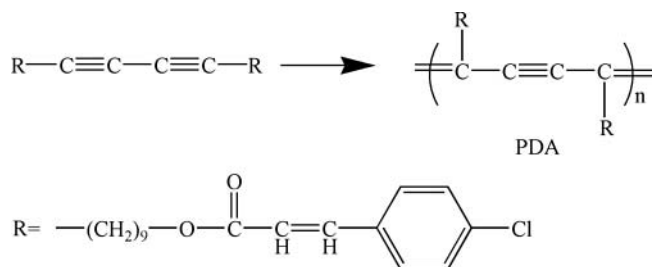


Fig. 1. Chemical structure of the Cl-Cin-22 monomer and the resulting polydiacetylene.

ca. 2×10^{-10} Torr. A differentially pumped He I lamp (21.2 eV) was used as an excitation source, and photoelectrons were detected with a concentric hemispherical analyzer in fixed analyzer transmission mode using a pass energy of 2 eV. The sample stubs were held at ca. -6.3 V relative to ground during UPS analysis in order to measure the low kinetic energy portion of the spectra.

3 Results and Discussion

A film of Cl-Cin-22 monomer was spin-coated onto a quartz substrate and exposed to He I radiation inside the ultra high vacuum (UHV) chamber and removed after various exposure times for UV-Vis analysis. Prior to exposure, the monomer film showed no significant absorbance peaks in the range of 400–900 nm and appeared transparent to the eye. UV exposure led to a blue-colored film with an

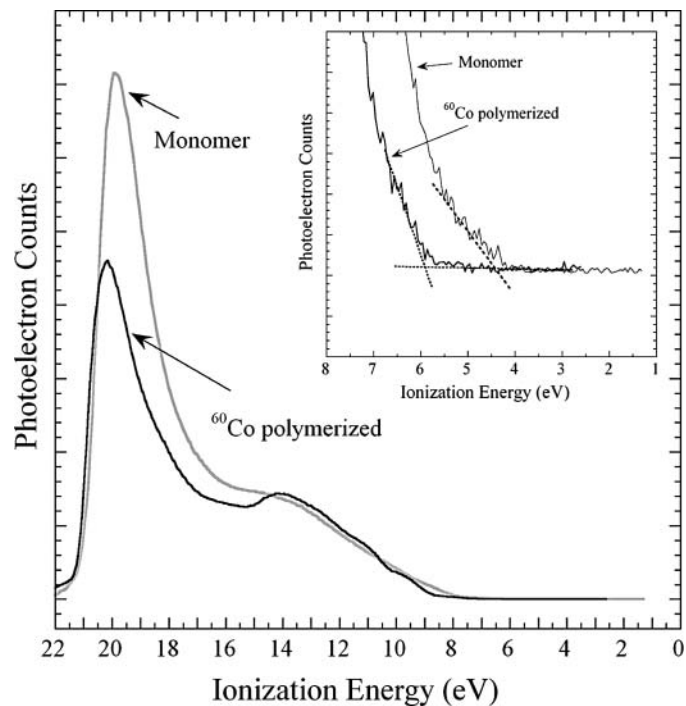
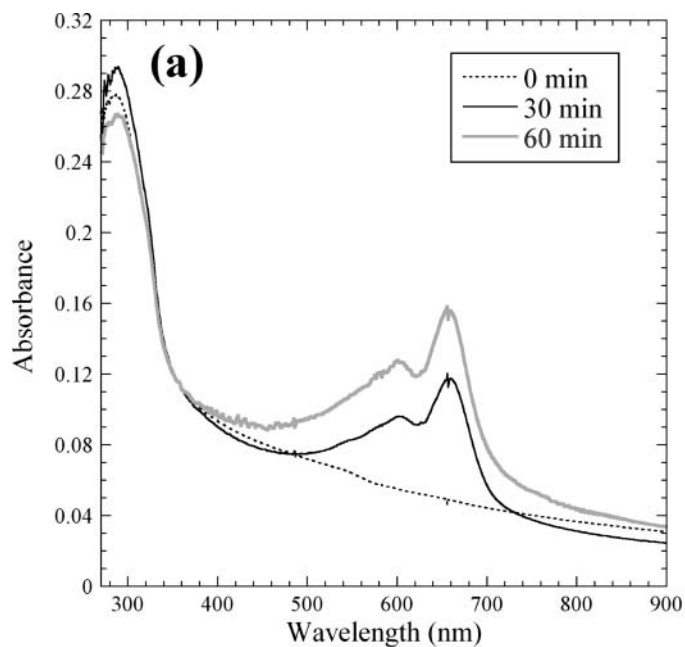


Fig. 3. He I UPS of spin coated Cl-Cin-22 monomer and ^{60}Co γ radiation polymerized sample, with the inset showing expansion of the threshold region.

absorption maximum near 660 nm that increased in intensity with exposure, as shown in Figure 2(a). The structure in the spectrum in Figure 2a indicates a spacing of 1515 cm^{-1} . This spacing suggests a coupling of the conjugated chain

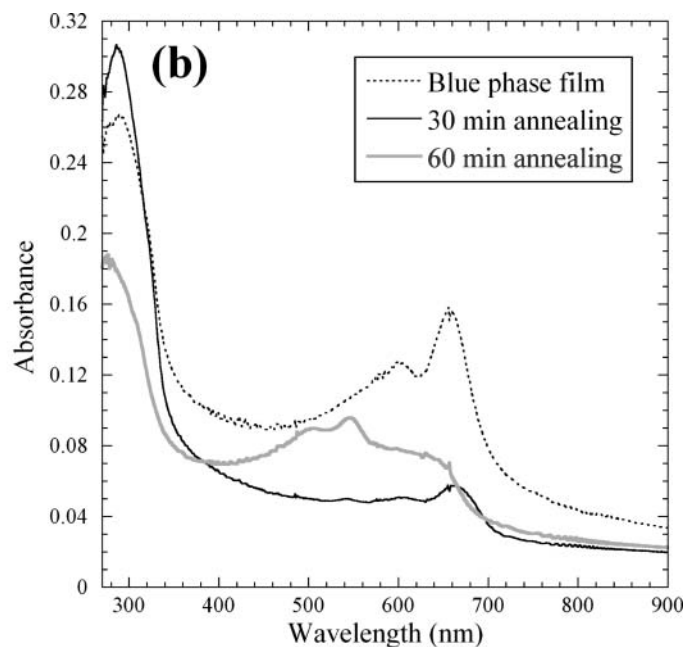


Fig. 2. UV-Vis absorbance spectra of a spin-coated film of Cl-Cin-22 monomer on a quartz slide. a) Absorbance as a function of He I radiation exposure time; b) Absorbance of a 60 min He I irradiated film (blue phase) as a function of annealing time at 85°C in air.

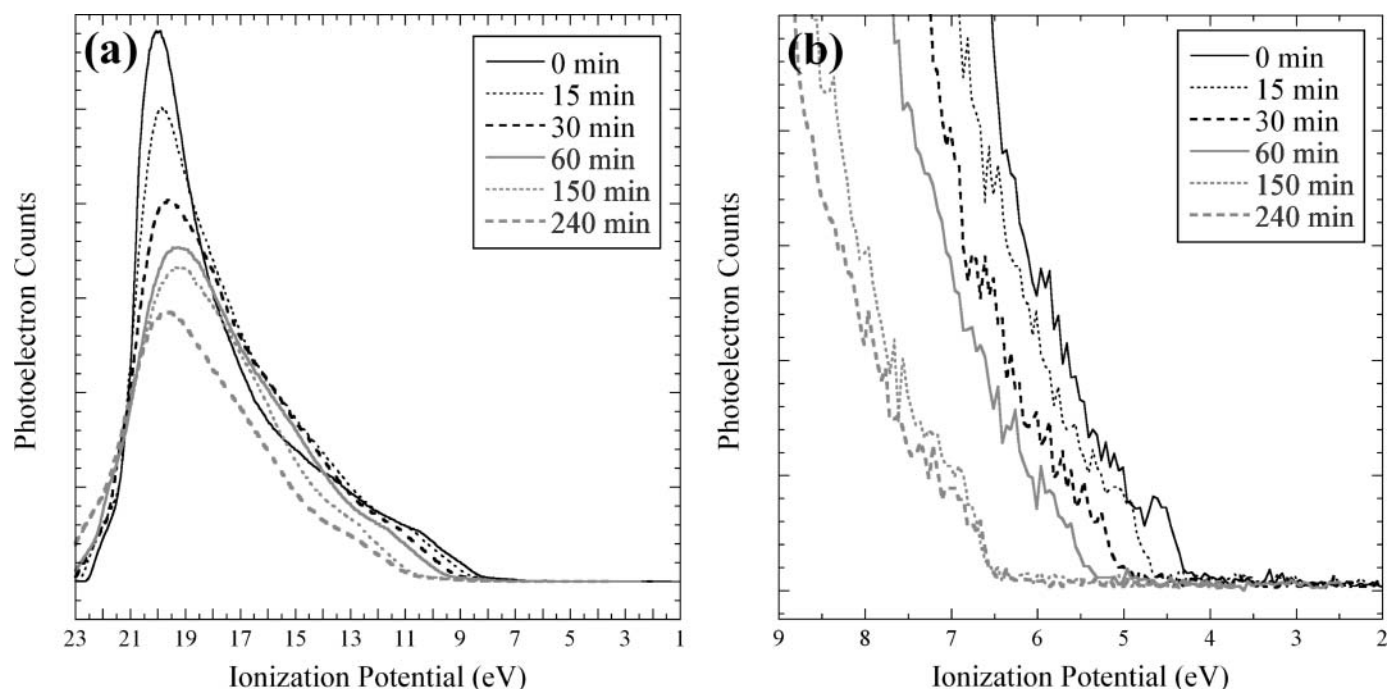


Fig. 4. UPS of PDA monomer as a function He I light exposure. Figure a) shows the entire spectra, and Figure b) displays expansion of the HOMO region.

double bond to the electronic state. Heating of this film at 85°C in air converted it to a red film with maximum absorption at 544 nm as shown in Figure 2(b), similar to previously reported results (7). The blue phase is metastable and appears during the course of the polymerization reaction; it eventually converts to a more stable red phase upon heating. In Figure 2, the absorption peak below 300 nm is due to the p-chlorocinnamate group (8).

Figure 3 shows UPS spectra of the Cl-Cin-22 monomer and ^{60}Co γ radiation-induced polymer films. The measured kinetic energy scale of the photoelectrons has been converted to ionization energy by setting the secondary electron cutoff of each spectrum to 21.2 eV. By this procedure, the vacuum level corresponds to an ionization potential of 0 eV. The threshold ionization potential is determined by linear extrapolation of the highest occupied molecular orbital (HOMO) peak to the base line, as shown in the inset of Figure 3. The solid-state threshold ionization potentials of the Cl-Cin-22 monomer and ^{60}Co γ radiation polymerized samples are 4.4 and 5.9 eV, respectively. The latter value agrees with previous reports of PDA ionization threshold energies (1, 3, 9, 10), with typical values of 5.1–5.7 eV. It is surprising that the apparent threshold ionization energy of the monomer is lower than that of the polymer, since one would expect greater delocalization of the valence electronic states to result in lower ionization energies. The possibility of surface charging being responsible for the apparently low ionization threshold of the monomer film may be excluded, since this would lead to artificially high ionization energies. It is likely that exposure of the

monomer to the 21.2 eV radiation initiates polymerization to the blue phase as shown in Figure 2.

In order to investigate the possibility that UV-induced decomposition/polymerization may be responsible for the unexpected result, an experiment was performed in which the Cl-Cin-22 monomer film was continuously exposed to He I radiation while spectra were collected. Figure 4 displays UPS spectra of PDA monomer as a function of radiation time. As shown, the threshold ionization potential of the material increases with exposure time, with an initial value of 4.6 eV ($t = 0$) and a final value of 6.7 eV ($t = 240$ min). This suggests that polymerization is not primarily responsible for the observed increase in the threshold value, since it would cause the value to *decrease*. It is possible that the data in Figure 4, up to 30 min, involve the ionization of a blue phase under a mechanical strain. That strain may be slowly relieved as the film converts to a red phase and also undergoes degradation of the conjugated chain. Hence the ionization energy increases. Note that the ionization energy of the thermochromic PDA increases as mechanical strain is partially relieved (3).

To gain further insight, UPS spectra of p-chlorocinnamic acid and its dimer (bis-p-chlorotruxinic acid) have been observed and are shown in Figure 5. The inset shows expansion of the HOMO region, indicating threshold ionization potentials for p-chlorocinnamic acid and bis-p-chlorotruxinic acid of 4.8 eV and 6.7 eV, respectively. Similar to the results for PDA-Cl-Cin-22 and its monomer, the dimer exhibits a *larger* ionization potential threshold. Degradation of PDA-Cl-Cin-22 on exposure to 254 nm

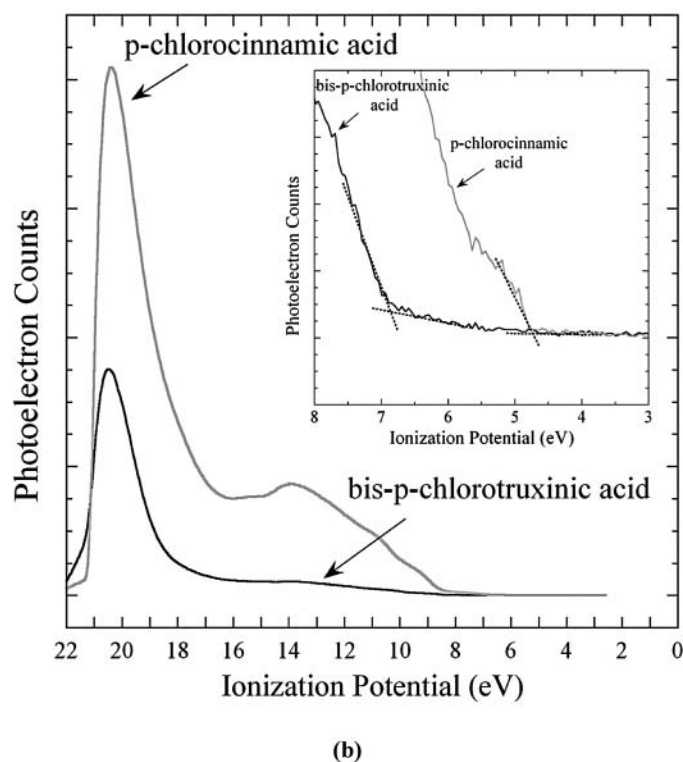
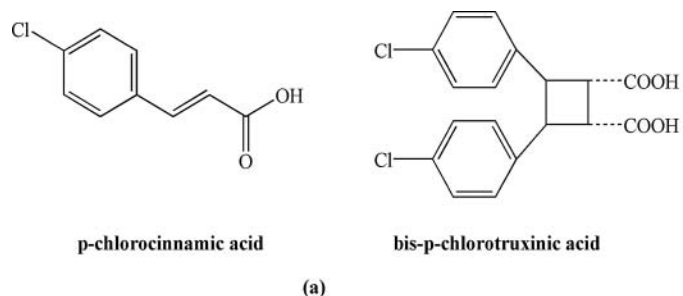


Fig. 5. a) Chemical structure of p-chlorocinnamic acid and bis-p-chlorotruxinic acid and b) He I UPS of p-chlorocinnamic acid and bis-p-chlorotruxinic acid with the inset showing expansion of the threshold region.

light has been previously reported (7), although UPS studies were not performed.

4 Conclusions

Polydiacetylenes of the bis-p-chlorocinnamate of 10,12-docosadiyn-1, 22-diol (Cl-Cin-22) have been investigated

by UV-Vis and UPS. A metastable blue phase is observed during continuous exposure of a spin-coated monomer film to 21.2 eV radiation. The threshold solid state ionization energy of a ^{60}Co γ polymerized sample is 5.9 eV, consistent with earlier UPS studies of PDA. An increase in ionization potential energy as a function of He I radiation exposure has been observed on a spin coated monomer film as a function of time. This suggests that irradiation can initiate surface polymerization as well as eventual degradation of the material. A higher ionization potential has been recorded on bis-p-chlorotruxinic acid as compared to p-chlorocinnamic acid films.

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