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Studies of the Polydiacetylene Bis-p-chlorocinnamate of 10,12-Docosadiyn-1,22-diol

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The bis-*p*-chlorocinnamate of 10,12-docosadiyn-1,22-diol polymerized with ^{60}Co gamma radiation to give a soluble polydiacetylene (PDA), PDA-ClCIN-22. We have studied PDA-ClCIN-22 in both crystallographic powder and solution coated films. Thin films of solution coated PDA-ClCIN-22 exhibit an absorption maximum of 544 nm, similar to the concentrated solution in chlorobenzene. Irradiation of these films with 254 nm UV light in air leads to loss of intensity in the visible spectrum. The thin films of PDA-ClCIN-22 are amorphous by X-ray powder diffraction. Irradiation of both PDA-ClCIN-22 powder and film with 254 nm light did not result in photochemical reactivity of the chlorocinnamate group as recorded by FTIR spectra. Differential scanning calorimetry (DSC) studies of PDA-ClCIN-22 reveal that presence of monomer and endothermic transitions near 116°C and 134°C on a first heating. On a second heating of a sample of PDA-ClCIN-22 taken to 150°C on first heating, the 116°C and 134°C endotherms are absent. These endotherms are also lost by monomer extraction with boiling cyclohexane. One possible source of the endotherms would be conformational transitions in the side chain.

Keywords: PDA ClCIN-22, ^{60}Co gamma radiation, ultraviolet degradation

1. Introduction

The molecular structure of bis-*p*-chlorocinnamate of 10,12-Docosadiyn-1,22-diol (PDA-ClCIN-22) whose synthesis and preparation is described in 1993 by Sandman et al, is given in Figure 1 (1–3). It is also reported that after the monomer ClCIN-22, which is thermally stable, is polymerized by ^{60}Co γ-radiation the color of the solid becomes coppery brown (1).

The X-ray powder diffraction of ClCIN-22 which has the en-yne backbone structure, exhibits a reflection at $d = 4.91$ Å (1). The absorption maximum of the diluted solution of PDA, which has *p*-chlorocinnamate as a side group, depends on the refractive index of the solvent and points out the sensitivity of the conjugated backbone for the local solvent environment (2).

The optical absorption spectra and electronic structure and properties of PDA-ClCIN-22 have been studied in earlier reports (3, 4) and, in PDA-ClCIN-22 the lowest-energy photoexcitations are excitons with a binding energy of nearly 0.5 eV, is reported (4).

In the present study, the bis-p-chlorocinnamate polymerized with ^{60}Co gamma radiation to give a soluble polydiacetylene (PDA), PDA-ClCIN-22, which is characterized with different techniques such as ultraviolet/visible spectroscopy, Fourier transform infrared spectroscopy and differential scanning calorimetry.

2. Experimental

2.1. *Materials and methods*

The synthesis of Bis-p-chlorocinnamate of 10,12-Docosadiyn-1,22-diol (ClCin-22) is clearly described by Sandman et al. (1). The bis-p-chlorocinnamate was polymerized with ^{60}Co gamma radiation with 50 Mrad for 64 h to give a soluble polydiacetylene (PDA). PDA-ClCIN-22 is studied in both crystalline powder and solution coated films.

UV-visible absorption spectra were measured with a UV/Vis/NIR spectrometer (Perkin-Elmer Lambda-9). Two different samples were prepared to see the difference and make the comparison easier. First one is prepared with ClCIN-22 monomer (100 mg) and polystyrene (50 mg) dissolved in chloroform (5 ml). This solution is spin coated (with 500 RPM for 30 sec) on glass as a thin film. Before irradiation and after each irradiation of the sample with 254 nm UV light (with the presence of air) for 30 sec., 1, 2, 3, 4, and 5 min, the UV-Vis absorption spectra were measured (between 320–900 nm). As a second sample, the PDA-ClCIN-22 (100 mg) which is polymerized with ^{60}Co

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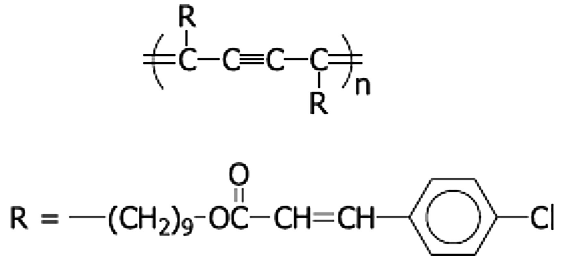

Fig. 1. The molecular structure of PDA-ClCIN-22.

gamma source and polystyrene (50 mg) are dissolved in 5 ml chloroform. After the solution is spin coated (with 500 RPM for 30 sec) on glass, it is irradiated for 2, 4, and 5 min. UV-Vis absorption spectra were measured before irradiation and after each irradiation.

The FTIR measurements were done with a Perkin-Elmer FR-1000 Paragon Instrument. The samples for FTIR measurement were prepared in two different ways. The first one is prepared with the solution of PDA-ClCIN-22 in chloroform. This solution is spin coated on a KBr disk with 500 RPM for 30 sec and put in a vacuum oven for 2 h. The second sample is prepared as a pellet with KBr powder and PDA-ClCIN-22. Both samples were irradiated with 254-nm light and FTIR spectra were measured. FTIR spectra of the pellet were also measured after heating at 130°C for 2 h. All the FTIR measurements were done with the resolution of 2 cm^{-1} 64 scans.

A DSC Q 100 instrument was used for the measurements. For DSC measurements, first PDA-ClCIN-22 powder was used as a sample. After that, the PDA-ClCIN was mixed with hot cyclohexane (3 ml) and the solvent removed. There were two DSC measurement cycles and both were performed before and after monomer extraction. The first DSC measurement cycle was heating from −90°C to 250°C at a rate of 10°C/min and the second DSC measurement cycle was heating from −90°C to 180°C at a rate of 10°C/min and the given thermal cycles were run twice for each sample.

3. Results and discussion

In Figure 2, times of 254 nm UV irradiation are given. Thin films of solution coated PDA-ClCIN-22 exhibit an absorption maximum of 544nm (Figure 2), similar to the concentrated solution in chlorobenzene (2). Irradiation of these films with 254 nm UV light in air leads to loss of intensity in the visible spectrum. In the case of spin coated monomer films, UV irradiation leads to films with significantly lower absorbance than the films in Figure 2. Prolonged UV irradiation leads also to loss of intensity.

FTIR measurements were performed before and after UV irradiation and heat treatment with the presence of air, in order to determine any changes in the vibrational modes of the molecular bonds. After heating at 130°C, the

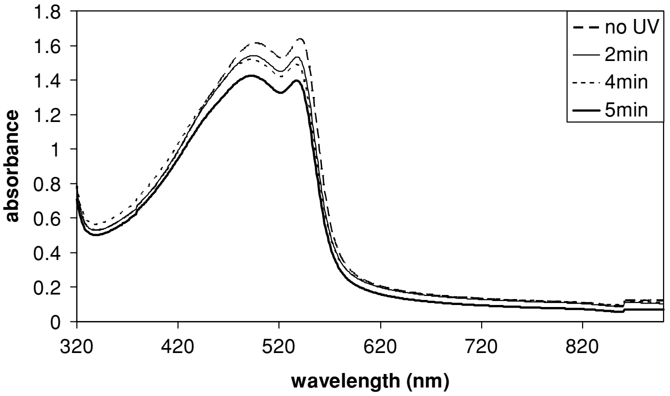

Fig. 2. UV–visible absorption spectra of PDA-ClCIN-22, coated from chloroform solution; times of irradiation at 254 nm are given.

FTIR spectra revealed changes at 2800–3000, 1150–1350, and 400–650 cm^{-1}, regions associated with CH vibrations. These differences suggest changes in the conformations associated with the CH_2 groups.

Irradiation of both PDA-ClCIN-22 powder and film with 254 nm UV light did not result in photochemical reactivity of the chlorocinnamate group as recorded by FTIR spectra.

Differential Scanning Calorimetry measurements were done to confirm the presence of monomer in PDA-ClCIN-22. It is understood that the PDA-ClCIN-22 which was polymerized with ^{60}Co gamma source includes monomer as revealed by thin layer chromatography of extracts. In order to show that with DSC first the sample of PDA-ClCIN-22 is taken to 250°C which is higher than the melting point of polymer, both before and after monomer extraction. Following to this, a new sample is taken to 150°C which is lower than the melting point of polymer (near 166°C), again before and after monomer extraction.

Differential scanning calorimetry (DSC) studies of PDA-ClCIN-22 reveal the presence of monomer and endothermic transitions near 116°C and 134°C on a first heating. On a second heating of a sample of PDA-ClCIN-22 taken to 150°C on first heating, the 116°C and 134°C endotherms are absent. These endotherms are also decreased by monomer extraction with boiling cyclohexane.

4. Conclusions

DSC suggests metastable side chain conformations in methylene $[(CH_2)_9]$ group and the thin films of PDA-ClCIN-22 are amorphous by X-ray powder diffraction. Irradiation of both PDA-ClCIN-22 powder and film with 254 nm light did not result in photochemical reactivity of the chlorocinnamate group as observed by FTIR spectra. One interpretation of the FTIR and DSC is that gamma radiation polymerization of the ClCIN-22 monomer leads to a PDA whose side groups are in conformations other than the low energy staggered one. Heating of these metastable species likely leads to staggered conformations in the side groups, and a loss of the weak endothermic phase transitions in the DSC. This point has not been previously stressed in the PDA literature. Changes in the FTIR spectra in the absorptions of the CH_2 groups were previously noted in studies of the thermochromic PDA-ETCD (5) and related PDA segmented copolymers (6). In order to detect the presence of higher energy side chain conformations in this PDA, crystal growth of single crystals of ClCIN-22 is in progress.

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