

Optical properties of polyazomethine with oxygen atom in the backbone

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Received 21.04.2008; published in revised form 01.08.2008

ABSTRACT

Purpose: The aim of this paper is to show results of optical measurement performed on poly – (1-(4-methylenephenoxy-1)phenylene-4-methylene-1,4-phenylenitrylomethylene) (PPI2) polyazomethine thin films and to compare with poly - (1,4-phenylenemethylenenitrilo-1,4 phenylenitrylomethylene) (PPI).

Design/methodology/approach: Influence of oxygen atom in the polymer chain on optical properties of polyazomethine was investigated. Optical UV-VIS and FTIR absorption spectra of polyazomethine PPI2 with oxygen atom were recorded and X-ray patterns of these polymers were performed.

Findings: The oxygen atom incorporated in ordered way into PPI2 chain breaks conjugation and cause increase of energy gap in polymer.

Research limitations/implications: The oxygen atom incorporated between phenylene rings of dialdehyde changes PPI chain into sequence of alternative three ring conjugated fragments and oxygen atoms.

Practical implications: Addition of oxygen atom inside aldehyde fragment in polyazomethine chain influences conformation of polymer. The prepared layers of polyazomethine with oxygen atom in the backbone are expected to be more amorphous and more luminescent properties.

Originality/value: Polyazomethine is very interesting material as it has nitrogen atom in the backbone, and is isoelectronic counterpart of polyparaphenylenevinylene (PPV). This paper shows that addition of oxygen atom into polyazomethine chain influences its optical properties.

Keywords: Conjugated polymer; Ether group; Energy gap; UV-VIS absorption spectroscopy; FTIR spectroscopy

PROPERTIES

1. Introduction

Polyazomethine 1,4-phenylenemethylenenitrilo-1,4-phenylenitrylomethylene (PPI) is widely enough described material [1-5], suitable for optoelectronic or photonic applications, being isoelectronic counterpart of polyparaphenylenevinylene PPV [6].

The aim of this paper is to present new polyazomethine PPI2, prepared via chemical transport method (CVD) [7-10] by polycondensation of 4,4'-oxydibenzaldehyde ODBA and para-phenylenediamine PPDA. It is interesting to compare optical properties of both polyazomethines.

2. Materials and technology

2.1. Reaction and CVD process

Polyazomethine thin films were prepared by polycondensation of PPDA and ODBA following the reaction as below (Fig. 1):

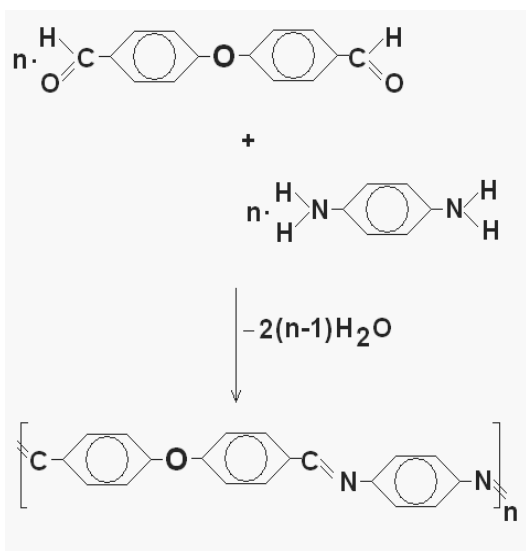


Fig. 1. Scheme of polyazomethine PPI2 polycondensation

As result of reaction $-C=N-$ double bond between monomers is formed, the polymer chain becoming longer and longer, with one water molecule being released at each step. Water molecules were removed by rotary pump and process was carried out under low vacuum (10^{-1} Tr). The stream of neutral gas Ar used as a carrier agent was forked into three equal streams flowing around the crucibles with relevant monomer. The temperature of ODBA was 80°C while that of PPDA was equal to 84°C . Next, the streams entered the colimator where they merged into one stream which transported mixed monomers molecules towards the substrate situated over an opening of the stream collimator. PPDA diamine was purchased from ALDRICH, while ODBA was synthesized in the Institute of Macromolecular Chemistry of Romanian Academy of Sciences in Iasi, Romania.

2.2. Experimental

Polyazomethine thin layers were deposited onto BK7 glass, KBr or quartz substrate at room temperature. The thickness of prepared films was about 100, 200 or 300 nm depending on time of deposition. Optical UV-VIS absorption spectra were recorded with JASCO UV-VIS-NIR spectrophotometer within 200-2500 nm wavelength interval. Diffraction patterns were taken on X-Ray Diffractometer TUR M-62. FTIR spectra was recorded with FTIR spectrophotometer FTS40A BIORAD within $400-4000\text{ cm}^{-1}$ range. All measurements were performed at room temperature.

3. Results

3.1. UV-VIS measurements

The absorption spectrum of PPI2 thin film with oxygen atom in the backbone deposited onto quartz substrate is shown in Fig. 2, as reference PPI absorption spectrum being added.

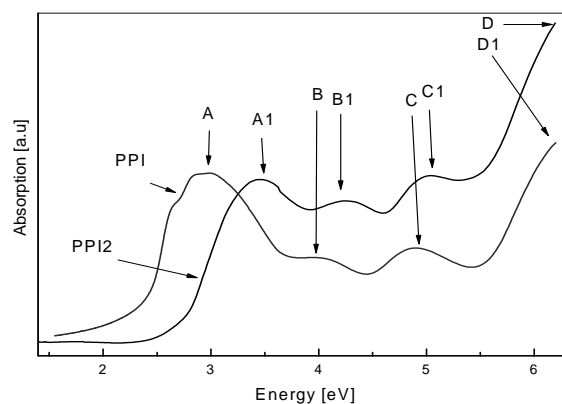


Fig. 2. UV-VIS absorption spectra of polyazomethine PPI and polyazomethine PPI2

Four bands in polyazomethine PPI2 spectrum are peaking at about $3,48\text{eV}$ (A), $4,25\text{eV}$ (B), $5,03\text{eV}$ (C) and $6,20\text{eV}$ (D). Maxima of bands in PPI spectrum are at about $2,95\text{eV}$ (A), 4eV (B), $4,93\text{eV}$ (C), $6,2\text{eV}$ (D).

3.2. FT-IR measurements

FTIR spectrum of PPI2 thin film deposited onto KBr substrate is shown in Fig. 3, the spectrum of PPI layer being added for comparison.

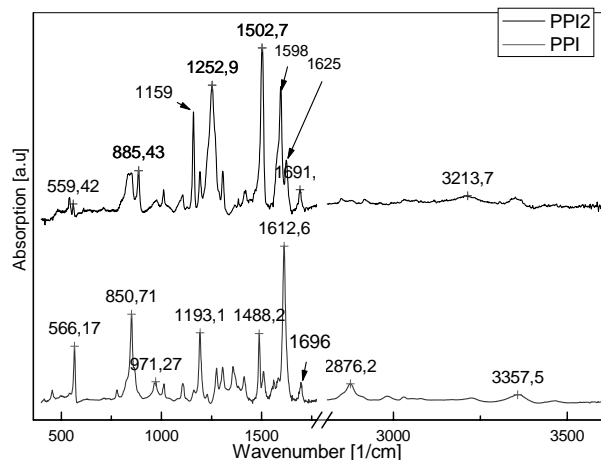


Fig. 3. FTIR absorption spectrum of PPI 2 and PPI

Most important features in both spectra are seen within 800-1700 cm^{-1} wavenumber interval. The strongest peaks in PPI2 spectrum are at about 1159, 1252.9, 1502.7, 1598 and 1625 cm^{-1} . Additionally, weak peaks are seen at about 885.4, 1687 and 3213.7 cm^{-1} .

The strongest peak in PPI spectrum is seen at about 1612.6 cm^{-1} , and small ones at about 2876.2 and 3357.5 cm^{-1} .

3.3. X-ray measurements

X-ray diffraction pattern performed on polyazomethine PPI2 thin film deposited onto BK-7 glass substrate is shown in Fig. 4, as reference PPI pattern is added. Two low intensity peaks at about 19.24 and 23.14 degrees superimposed onto broad amorphous background are seen in PPI2 diffraction pattern. The intensity of these peaks is much lower than intensity of PPI peaks at about 20.74 and at 23.5 degrees.

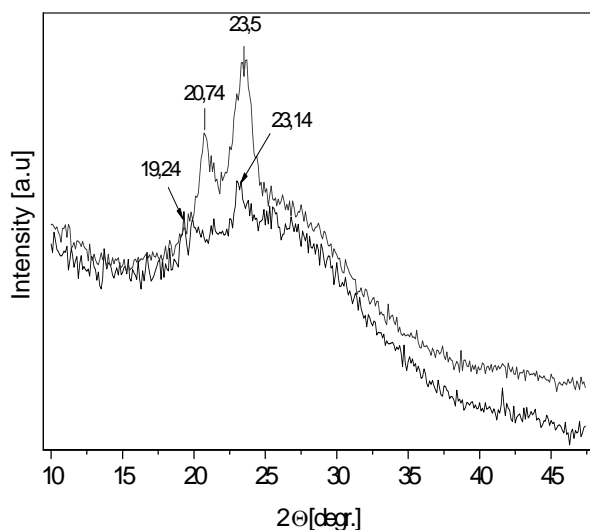


Fig. 4. X-ray diffraction pattern of PPI and PPI2 thin films

4. Discussion

Four bands seen in PPI2 absorption spectrum are attributed to $\pi - \pi^*$ type electronic interband transitions. A1 band is due to interband transitions connecting HOMO and LUMO delocalised states of PPI2 polymer. This band is of the same origin as A band of PPI but it is shifted on 0.53 eV to the higher energy because oxygen atom incorporated in ordered way into PPI chain bring about shortening the length of conjugated fragments in PPI2 backbone. Oxygen atoms between benzene rings of aldehyde fragments make that the conjugated fragments in PPI2 are limited to three benzene rings entities distributed alternately with oxygen atoms along with the polymer chain, as it can be seen in Fig. 5.

The intensity of A1 band due to delocalised transitions relatively to intensities of B1 and C1 bands lower than is the intensity of A band with respect to band C ones in PPI spectrum. That means, not only the conjugation length is shorter, but also PPI2 polymer chain is more twisted than the chain of PPI. The B1

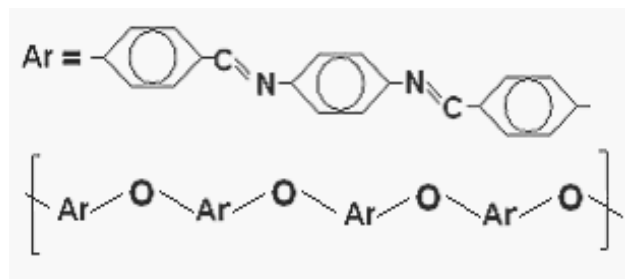


Fig. 5. PPI2 chain with alternate oxygen atoms and three benzene entities

band is attributed to bound Frenkel exciton connected with interband transitions connecting delocalised valence states and localised conduction states and vice versa, while C1 band being due to non bound electron hole pairs connected with transitions between these states. The B1 and C1 bands in PPI2 spectrum correspond with bands B and C in the PPI spectrum. The D1 band with maximum at 6,2 eV is connected with transitions between localised states on benzene rings. One can see that its intensity is nearly the same as that of D band in PPI, the number of localised state in both polymers being comparable. This is thought to go with neraly coincidence D1 and D bands in the two spectra. Additionally, this is corresponds rather well with observed displacements A1 and B1 bands with respect with those of A and B bands, which have appeared to be larger for transitions linking two delocalized states than for delocalised-to-localised type ones.

FTIR spectra correspond rather well with above considered UV-VIS spectra. One can see two strong enough peaks at about 1159 and 1252.9 cm^{-1} , which are attributed to C-O and C-O-C vibrations of ether groups constituted in PPI2 by benzene rings separated by oxygen atom in each aldehyde related fragment of the chain [11-13]. The intensity of rather strong enough 1192 cm^{-1} peak related to valence backbone vibrations is considerable suppressed in PPI2 spectrum, which is attributed to decrease in the conjugation length related to oxygen atoms in PPI2 chain. Peaks at about 1502 and 1598 cm^{-1} are related with benzene ring vibrations and rather short conjugation length in case of PPI2 chain. The latter 1598 cm^{-1} peak frequency is not very different from 1595 cm^{-1} vibrations of benzene ring indicating PPI2 polymer chains not being too long. The presence of 1625 cm^{-1} peak is some confirmation of polyazomethine $-\text{C}=\text{N}-$ double bonds forming in polycondensation polymerisation. While comparing its intensity with that of the strongest peak in PPI spectrum at about 1612.6 cm^{-1} , one can see that conjugation length in PPI2 is much shorter than that in PPI. Moreover, it is thought that some asymmetry of its shape may indicate on smaller number of vibrations due to benzene rings ending polymer chains. The 1691 cm^{-1} peak is attributed to $\text{C}=\text{O}$ groups and its intensity is similar to that of 1696 peak in PPI, which mean that terminal groups are not too numerous in both polymers. Similarly, rather small intensities of weak features at about 3213 cm^{-1} make additional indication of rather small impact of terminal $-\text{NH}_2$ groups on the spectra, so that one may expect that chains of both polymers are sufficiently long.

While comparing diffraction patterns from PPI2 and PPI one can expect that the latter ones are more ordered or they reveal

higher degree of crystallinity. There the location of PPI peaks correspond rather well with those reported by Proń [15] for powder samples.

The average size of PPI grains is about 130 Å, while grain's size in PPI2 thin films being about 30-40 Å. More amorphous polymer is expected to be more suitable luminescence properties.

5. Conclusions

Absorption edge and the first delocalised band in UV-VIS absorption spectrum of polyazomethine PPI2 is shifted to higher energies with respect to PPI spectrum. It is connected with lower conjugation length in PPI2 than in PPI chain.

Additional strong peak at 1502.7 cm⁻¹ in FT-IR spectrum and is attributed to presence of oxygen atom. The 1625 cm⁻¹ peak is due to forming -C=N- double bond and its intensity is lower than the same peak in PPI spectrum.

X-Ray spectra showed difference in degree of crystallinity of compared polyazomethines. The intensity of peaks is lower, and first peak in PPI2 pattern is shifted into lower 2θ angle value. It is attributed to higher amorphous properties of PPI2 and smaller grain sizes.

The presence of ether group in the aldehyde fragment of polymer caused increase of energy gap and increase of amorphous properties.

These differences could be the reason for better luminescence of polyazomethine.

Luminescence spectra of polyazomethine PPI2 will be carrying out in the nearest time.

Acknowledgements

This work has been financially supported by the European Social Fund (EFS) in the framework of project No. Z/2.24/II/2.6/17/04 and KBN grant (Poland), No. 3 T08E 040 26 and in cooperation with Institute of Macromolecular Chemistry in Romanian Academy of Sciences in Iasi in Romania.

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