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Influence of technological conditions on electronic transitions in chemical vapor deposited poly(azomethine) thin films

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Abstract

Thin films of poly(1,4-phenylenemethilidynenitrilo-1,4-phenylenenitrilomethilidyne) (PPI) have been prepared by chemical vapor deposition in the horizontal geometry using gaseous argon as a transport agent. PPI thin films have been grown by polycondensation of *para*-phenylene diamine (PPDA) and terephtal aldehyde (TPA). Fourier Transform Infrared spectra confirm formation of PPI layers without end groups. The strongest absorption band with discernible vibronic progression has been found to be due to superposition of 2.64, 2.82 and 3.03 eV bands corresponding to interband transitions connecting electronic ground state and vibrational levels of electronic excited state. A feature seen at about 2.6 eV in the spectra of PPI films prepared at higher temperatures of PPDA and TPA sources are attributed to excitons connected with the $\pi-\pi*$ gap. Shoulder at 3.31 eV is attributed to interband transitions between delocalized states, while a peak at 4.2 eV is attributed to excitons formed by localized holes and delocalized electrons and vice versa and interband transitions connecting delocalized and localized bands, with the binding energy of about 0.8 eV. Thin films prepared at low temperatures of monomers consist of randomly distributed PPI chains weakly bound together.

Keywords: Polymer thin films; Polyazomethine; Chemical vapor deposition; Electronic transitions

1. Introduction

Aromatic poly(azomethines), known also as the Schiff bases [1,2], belong to alternately conjugated polymers with nitrogen atoms in the backbone. Since many years this polymer family has been of interest for their good thermal stability and interesting opto-electronic properties [1–3]. Some poly(azomethines) have been prepared by solvent-based polymerization and their thin films have been deposited by spin-on technique [1–7]. However, applicability of this technique is limited only to soluble polymers and in order to prepare thin films of insoluble poly(azomethines), the thermal vacuum evaporation or chemical vapor deposition (CVD) methods based on polycondensation have been used [3,8–12]. It is worth mentioning that thermally vacuum evaporated films, similarly like those prepared by CVD, are free from unintentional impurities that cannot be avoided in the case of solvent-based polymerization or spin-on coating techniques [3,8–12]. The simplest representative of poly(azomethines) is 1,4-phenylene-methylidynenitrilo–1,4-phenylenenitrilomethylidyne, which hereafter will be referenced as PPI [1]. PPI has the backbone consisting of alternately repeating para-phenylene and azomethine dimers. Being an isoelectronic counterpart of poly (para-phenylene vinylene), PPI has been expected to be suitable for photovoltaic and other optoelectronic applications [3,4,8–12]. The aim of this work is to find how the electronic properties of PPI thin films formed by CVD are affected by technological conditions of their preparation. Our interest in studying the CVD prepared PPI thin films is also to better understand mechanisms of condensation polymerization process running at the interface of the vapor/solid phase, structure and morphology of as-deposited films as well as the electronic structure of polymers having nitrogen atoms in the backbone.

2. Experimental details

The starting materials, i.e. para-phenylene diamine (PPDA) and terephthal aldehyde (TPA) monomers, have been purchased

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from Aldridge. High purity Ar has been used as a transport agent in the CVD technique applied to PPI thin films deposition. In the CVD process used, the argon stream was divided into two or three equal streams, two of them were flowing over boats containing PPDA and TPA heated to relevant temperatures (Table 1). Then, the two- or three-streams merged into one for the transported monomers molecules approaching reaction chamber to be mixed up. In the reaction chamber, monomers molecules, transported by the Ar stream, impinged onto the BK-7 glass substrate kept at room temperature and PPI thin films were grown on the substrate via polycondensation of PPDA and TPA. Plates of pressed KBr were used as a substrate for Fourier Transform Infrared (FTIR) measurements. FTIR spectra have been taken on a FTS-40A FTIR Biorad spectrometer operating in the range 700–4500 cm^{-1}. The structure of as-deposited PPI films have been examined with a conventional θ–2θ, TUR-M62, X-ray diffractometer using the Ni-filtered Cu K_α radiation. Morphology and roughness of film surfaces have been examined with an Explorer TopoMetrix atomic force microscope (AFM) working in the contact mode in the constant force regime. AFM images were obtained using a commercially available Si_3N_4 V-shape cantilever (force constant −0.032 N/m) with a tip radius <50 nm (TopoMetrix SFM probe model 1520-00). The UV–VIS spectra of PPI films deposited on BK-7 glass have been taken on a Beckmann spectrophotometer within the 270–900 nm wavelength interval. The film thicknesses, shown in the last column of Table 1, have been estimated by means of an interference microscope with an uncertainty of about ±50 nm.

3. Deposition of PPI thin films

3.1. Conditions of PPI thin films preparation

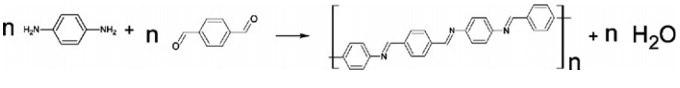
PPI thin films have been prepared by the CVD technique in the horizontal geometry via polycondensation process of PPDA and TPA, with Ar as a transport agent. Argon has been dosed into the CVD system by means of an adjusting screw of the working gauge of the pressure regulator mounted on an argon reservoir and the flow rate has been measured with a rotameter. The Ar stream, with a fixed flow rate controlled by a pressure regulator, has been forked into two or three equal streams, one flowing over a boat containing PPDA and the other over a boat with TPA, while the third one, if used, it has been argon itself. Technological conditions applied for preparing some representative films are presented in Table 1. It can be seen that, in the two-stream regime, the PPDA source temperature, T_{PPDA}, has been about 335 K in the case of films α and *b* and about 340 K for film *c*, while the TPA source temperature, T_{TPA}, has been fixed at 326 K which means that the temperature difference ΔT has been changed from 8 to 14 K. The flow rate has been fixed at about 80 l/min (films α, *b*) and about 150 l/min (film *c*). In the three-stream process (films *d–f*), T_{PPDA} has been equal to 334, 343 and 315 K for films *d*, *e* and *f*, respectively, while T_{TPA} was 326 K (films *d* and *e*) and about 315 K (film *f*), the flow rates being about 80 l/min (films *d* and *e*) and about 60 l/min for a film *f*. The substrate temperature has been kept equal to 298 K. Then, depending on the regimes used, two or three relevant streams have merged and one Ar stream transported mixed molecules of both monomers towards the inlet into the cylindrical reaction chamber of a much larger diameter. The inlet was centered on the axis of the cylinder chamber and the substrate holder fixed perpendicularly to the axis was situated at a distance d=4 or 5 cm from the inlet. Argon and reaction by-products or monomers that have not reacted have been removed from the reaction chamber with an exhaust rotary pump operating continuously during the deposition process.

Table 1
CVD operating parameters and thickness of PPI thin films

Film	T_{PPDA} (K)	T_{TPA} (K)	Total flow rate l/min	PPDA/Ar flow rate l/min	TPA/Ar flow rate l/min	Ar flow rate l/min	Time (s)	Gas inlet to substrate distance (cm)	Thickness (nm ±50 nm)
a	335	326	80	40	40	–	90	5	200
b	334	326	80	40	40	–	100	4	200
c	340	326	150	75	75	–	60	5	200
d	334	326	80	23.3	23.3	23.3	420	4	170
e	343	327	80	23.3	23.3	23.3	90	5	180
f	315	313	60	20	20	20	150	5	50

3.2. Kinetics of PPI film deposition

The process of CVD preparing PPI thin films by polycondensation of PPDA and TPA consists of three essential stages: the first, taking up molecules of both monomers by argon streams flowing over source boats filled with PPDA and TPA, respectively; the second merging together two or three argon streams into one associated with mixing molecules of the complementary monomers and their transport towards the substrate and the third, the adsorption of reagent molecules impinging onto the substrate. As it is CVD process, the film forming is thought to be due to polycondensation reactions running within the adsorption layer at the vapor/solid interface and resulting in the polymer chain formation [3]. While monomers mixture being carried by Ar stream towards the substrate, the polycondensation process should be postponed, which is equivalent to the positive Gibbs free energy ($\Delta G>0$). In fact, being equal to about 50 °C, the temperature of transported species has appeared sufficient for the reaction to be practically postponed as walls of the pipe transporting the reagent mixture remained clean. The polycondensation reaction driving the PPI film growth on the substrate kept at room temperature is as below which means that the reaction has



switched to the $\Delta G<0$ state at room temperature. As switching between the reaction postponing (monomers transport) and reaction progression (film deposition) conditions is connected with the temperature decreasing from 50 °C down to 25 °C, one