



Diphenylsilane-containing linear and rigid whole aromatic poly(azomethine)s. Structural and physical characterization

A. Tundidor-Camba^{a, e}, C.M. González-Henríquez^b, M.A. Sarabia-Vallejos^{c, d}, L.H. Tagle^a, P.A. Sobarzo^a, A. González^a, R.A. Hauyón^a, A.P. Mariman^a, C.A. Terraza^{a, e, *}

^a Research Laboratory for Organic Polymers (RLOP), Department of Organic Chemistry, Pontificia Universidad Católica de Chile, P.O. Box. 306, Post 22, Santiago, Chile

^b Laboratory of Nanotechnology and Advanced Materials (LNnMA), Chemistry Department, Universidad Tecnológica Metropolitana, P.O. Box 9845, Post 21, Santiago, Chile

^c Departamento de Ingeniería Estructural y Geotecnia, Escuela de Ingeniería, Pontificia Universidad Católica de Chile, Santiago, Chile

^d Instituto de Ingeniería Biológica y Medica, Escuela de Ingeniería, Pontificia Universidad Católica de Chile, Santiago, Chile

^e UC Energy Research Center, Pontificia Universidad Católica de Chile, Chile

ARTICLE INFO

Article history:

Received 20 April 2018

Received in revised form

6 July 2018

Accepted 14 July 2018

Available online 17 July 2018

Keywords:

Silylated-poly(azomethine)s

π -conjugation

Band gap values

Thermal stability

Conductivity

ABSTRACT

Six new whole aromatic poly(azomethine)s with different rigidity were prepared from three diamines and two dialdehydes, all of them containing a diphenylsilane moiety as a central structural element. Two amines containing biphenyl moieties were obtained for the first time. Thus, the synthesized polymers contain two silicon atoms in the repeat unit, where methyl and/or phenyl groups bonded to them, complete the tetra-valence of the heteroatom. The new materials were structurally characterized by means of FT-IR, solid NMR and elemental analysis. Solubility was tested in several organic solvents at room temperature and 40 °C and the inherent viscosity was determined. GPC analysis showed oligomeric chains of five repetitive units for the tested samples. Additionally, thermal behavior was studied by TGA and DSC analysis, by evidencing materials highly stable and rigid. Band gaps values ranging between 2.71 and 3.14 eV were obtained from UV/Vis and DRS analysis. The spin-coating technique was used to prepare films from soluble samples in NMP and their thicknesses were determined by the ellipsometric method. From these samples, and using AFM and four-point techniques, the effect of the annealing time on the roughness and conductivity of the films was studied. In accordance with the appropriate thermal and conductivity properties of the new silylated materials (which has a whole aromatic structure), could be proposed as an alternative for applications in the optoelectronics field.

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1. Introduction

Conjugated polymers based on C=C bonds or isoelectronic elements have been widely investigated and used as a semiconductor, LEDs (Light-emitting diodes) or photovoltaic cells in the last decades due to their intrinsic electrical properties [1]. These compounds are easy to process and their synthesis is low-cost compared to those silicon-based materials, which also present similar electrical properties. These advantages make this kind of conjugated polymers into excellent candidates for this purpose.

A common example of these materials are polymers which contain an imine functional group (–C=N–) in their structure, which are generically named poly(Schiff base)s or poly(imine)s. A particular type of these poly(imides)s are the so-called poly(azomethine)s (PAZMs), which are usually synthesized by condensation methodologies of primary amines and aldehydes. PAZMs with aromatic backbones are highly conducting polymers, which generates an excellent electrical performance when are included as functional components in material blends. Due to their extended π -system, they induce interesting properties to the whole material such as high thermal stability [2], excellent mechanical strength [3], and suitable optoelectronic properties for electrodes application [4]. At the same time, these polymers have been explored and tested for different applications in the field of organic electronic devices such as LEDs [5] and acid-sensors [6], among others [7,8].

* Corresponding author. Research Laboratory for Organic Polymers (RLOP), Department of Organic Chemistry, Pontificia Universidad Católica de Chile, P.O. Box. 306, Post 22, Santiago, Chile.

E-mail address: cterraza@uc.cl (C.A. Terraza).

Due to the presence of aromatic moieties, **PAZMs** are usually infusible and partially insoluble in common organic solvents [8], and several strategies have been applied to promote the processability of the material. With the aims to improve both, solubility and mechanical properties of **PAZMs**, the introduction of flexible elements in their backbone such as aliphatic units, several functional/pendant groups or structural irregularities, have been reported in the literature in the last years [9,10].

The aim of this research is the synthesis and the physical and structural characterization of conjugated oligomeric aromatic poly(azomethine)s. In order to overcome the solubility problems associated to the whole aromatic materials, we incorporated, in the repetitive unit, two silarylene moieties ($-\text{ArSi}(\text{R}_1, \text{R}_2)\text{Ar}-$) with methyl and/or phenyl groups as a lateral segment. Thus, the presence of silicon atom would promote a certain degree of flexibility to the chains due to the longer C-Si bonds compared to C-C ones. This fact and the nature of the R groups bonded to the heteroatom would allow to increase the solubility of the polymers in common organic solvents. Likewise, the silarylene units would promote semi-conduction in the materials due to the presence of $\delta-\pi$ conjugations in silicon internal orbital and also, due to the C=C neighboring conjugated system [11]. The polymers were characterized by Nuclear Magnetic Resonance (NMR) and elemental analysis. Material optical properties were measured via UV/Vis and diffuse reflectance spectroscopies (DRS) (optical absorption). The thermal properties of the **PAZMs** were studied using Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). In particular, the samples soluble in *N*-methyl-2-pyrrolidone (NMP) were deposited by spin-coating onto a pre-treated silicon wafer as substrate. Thicknesses of the deposited films were determined by ellipsometric methods, the refraction indexes of the layers, which are mandatory for performing ellipsometry, were obtained through an Abbe refractometer. The micro-topography of the film surface was performed via Atomic Force Microscopy (AFM). Besides, film conductivity values were also determined through four-point methodology. Thus, according to their thermal and electrical performance, the new synthesized silylated materials are a contribution in the optoelectronics field.

2. Experimental

2.1. Materials

Tetrakis(triphenylphosphine) palladium(0), bis(triphenylphosphine) palladium(II) dichloride, 4-aminophenyl boronic acid pinacol ester, 4-nitrophenyl boronic acid, anhydrous *N,N*-dimethylacetamide (DMAc), *p*-toluenesulfonic acid monohydrate (PTSA), anhydrous calcium sulfate, 10% w/w palladium on activated carbon and hydrazine monohydrate 80% w/w were obtained from Sigma Aldrich Chemical (Milwaukee, WI, USA). All other solvents and reagents were purchased commercially as analytical-grade (Sigma Aldrich Chemical, WI, USA or Merck, Darmstadt, Germany).

2.2. Instrumentation and measurements

NMR spectra (^1H , ^{13}C , and ^{29}Si) of the precursors and the new diamines were carried out in solution on a 400 MHz instrument (Bruker AC-200, Germany) using CDCl_3 as solvent and TMS as an internal standard. A Bruker DSX 200 spectrometer was used to obtain solid-state ^{13}C NMR spectra of the polymers at a frequency of 90.00 MHz with a commercial Bruker double air-bearing probe with 7 mm o.d. rotors. Chemical shifts were calibrated with glycine and are reported relative to TMS. Additionally, NMR spectra in CDCl_3 solution were recorded for the soluble polymers. FT-IR

spectra were recorded using KBr powder to manufacture sample pellets on a Perkin-Elmer (Fremont CA, USA) 1310 spectrophotometer over the range $4000-450\text{ cm}^{-1}$. The melting points were obtained with an SMP3 Stuart Scientific. Elemental analyses were made on a Fisons EA 1108-CHNS-O equipment (Thermo Scientific, Waltham/MA, USA). The inherent viscosity was measured in chloroform ($c = 0.5\text{ g/dL}$) in a Desreux-Bischof type dilution viscosimeter at $25\text{ }^\circ\text{C}$. The weight- (M_w), number-average molecular weight (M_n), the degree of polymerization (DP) and polydispersity index (PDI) of the oligomeric samples relative to polyethylene glycol standards were determined at $40\text{ }^\circ\text{C}$ using a GPC system 150cv (Waters, USA) equipped with a refractive index detector. For this, samples of **PAZM** dissolved in THF ($c = 0.5\text{ mg/mL}$) were refined using micro-pore filters of $2\text{ }\mu\text{m}$ mesh, then $100\text{ }\mu\text{L}$ of the drain solution was injected at 1 mL/min in a MesoPore column ($300 \times 75\text{ mm}$), useful for samples up $25,000$ molecular weight. Thermal behavior was analyzed through the determination of glass transition temperature (T_g) with a Mettler-Toledo (Greifensee, Switzerland) DSC 821 calorimetric system ($20\text{ }^\circ\text{C/min}$ under N_2 flow). The T_g values were obtained during the first heating scan under nitrogen gas atmosphere. Likewise, TGA measurements were carried out with a heating rate of $20\text{ }^\circ\text{C/min}$ under N_2 flow on a Mettler (Switzerland) TA-3000 calorimetric system equipped with a TC-10A processor, and a TG-50 thermobalance with a Mettler MT5 microbalance. For this, $6-10\text{ mg}$ of the polymer were placed in an alumina sample holder, and then, the TGA curves were performed between $25\text{ }^\circ\text{C}$ and $800\text{ }^\circ\text{C}$. The atomic percentage of carbon and nitrogen were determined with an elemental analyzer (Elemental Vario EL elemental analyzer; Elementar Analysensysteme, GmbH, Hanau, Germany). The absorption spectra of the polymers were recorded at room temperature, between 250 nm and 470 nm using a UV/Vis spectrophotometer model Lambda 35 (Perkin Elmer, USA) in NMP solutions ($c = 0.1\text{ mg/mL}$) and a slit of 0.5 . Diffusive reflectance measurement was carried out using a BaSO_4 standard white board in a UV-2450 UV-visible spectrophotometer. A spin coater, model KW-4A from Chemat Scientific, coupled with an oil-free vacuum pump (Rocker Chemker 410), was used for deposit the solution (polymer in NMP) over the pre-treated silicon wafer. This instrument possesses two spinning stages: (1) $500-2500\text{ rpm}$ ($2-18\text{ s}$) and (2) $800-8000\text{ rpm}$ ($3-60\text{ s}$) with tunable acceleration rate. The surface topography of the polymers was obtained by using an AFM model NTEGRA Prima, from NT-MDT Co., in intermittent contact mode at different scan ranges ($50 \times 50\text{ }\mu\text{m}^2$). Images were treated and analyzed using the off-line software Gwyddion. A Multi-angle laser Ellipsometer, model SE 400adv, from SENTECH Instrument GmbH, was used to perform optical measurements with variable incidence angle from 30° to 90° in steps of 0.5° , the equipment possesses an attached motorized goniometer, from Hüber Diffractionstechnik GmbH & Co. KG, for control incidence angle variation. A stabilized He-Ne laser ($\lambda = 633\text{ nm}$) permits a precision of 0.1 \AA in thin film thickness measurement. This equipment was used to obtain the thickness of the polymeric films. The four-point method was carried out using a digital multimeter from GW Instek, model GDM-8255, which includes the 4 W test lead for conduction measurement, as an optional accessory, used to obtain the material resultant voltage with high resolution ($0.012\% \text{ rdg} + 5$ digits). A DC power supply from GW Instek, model PLR 20-18, was used for administrating a constant current to the system (6 A).

2.3. Monomer synthesis

Synthesis and characterization of the silylated dialdehyde monomers (**6** and **7**) were reported in previous studies performed by our research group [9]. Briefly, the precursor bis(4-bromophenyl)di-R-silane ($\text{R} = \text{CH}_3$ or Ph) were obtained from the

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