



Effect of chemical structure and deposition method on optical properties of polyazomethines with alkyloxy side groups



P. Nitschke*, B. Jarzabek, A. Wanic, M. Domański, B. Hajduk, H. Janeczek, B. Kaczmarczyk, M. Musioł, M. Kawalec

Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 34 M. Curie-Skłodowska Str., 41-819 Zabrze, Poland

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ABSTRACT

Three (two novel) conjugated, thiophene phenylene based polyazomethines have been obtained parallel, by chemical vapour deposition (CVD) and by chemical synthesis. They were subsequently identified and characterised by an X-ray diffraction, thermogravimetric analysis, differential scanning calorimetry and detailed UV–Vis–NIR spectroscopy. Absorption spectra of the polymers' solutions and thin films have been examined. The spectra of polyazomethines without, with methoxy and with octyloxy side chains attached to the polymer backbone showed a conjugation-improving effect of alkyloxy side chain introduction. A comparison of spectra of the same polyazomethine's thin films deposited separately by spin-on and CVD methods revealed decrease in conjugation of compounds obtained during CVD. Additionally, amorphous character of the investigated thin films allowed to calculate the absorption edge parameters, in a way typical for amorphous semiconductor and to discuss their values in the context of chemical structure and deposition method. Surface imaging with atomic force microscope revealed different character of thin films deposited by spin-on and CVD methods.

1. Introduction

Polyazomethines, known also as Schiff bases or polyimines, with general structure $[R-CH=N-R']$, are a group of polymers exhibiting excellent thermal [1–7], mechanical [1,2] properties. Given the iso-electronic character of imine and vinylene bond [8], replacement of R fragments with aromatic (Ar), results in formation of a conjugated structure. Conjugated polyazomethines show interesting optical [1,3,4,7,9–16], optoelectronic [1,3,7,9–11,14–17] and electrical [1,7,18,19] properties. They also exhibit thermotropic liquid crystalline behaviour [20,21]. Apart from that, their synthetic methodology, which consists of a condensation polymerisation of a dialdehyde with a diamine, is very simple and may be proceeded in mild conditions. This is unlike Suzuki [22,23], Wittig [23,24], Stille [25] or Heck [26] carbon–carbon coupling protocols, commonly used for polymerisation of carbon–carbon linked conjugated structures. Products obtained from those protocols additionally require difficult purification from catalyst. Synthesis of polyazomethines on the other hand, may be catalysed with organic or mineral acids and the product may be purified by a simple precipitation. Due to synthesis and purification simplicity, conjugated polyazomethines are a considerable counterpart for currently employed conjugated structures in optoelectronic devices [7] such as photovoltaic cells [27], electroluminescent [3,23,28] or electrochromic [29,30]

devices. Such applications require however thin-film form. When highly aromatic polyazomethines are rather insoluble, their thin films may be obtained via gas-phase condensation by chemical vapour deposition (CVD) [28,30–35]. Another approach involves solubilisation by complexation of polyazomethine with Lewis acid or di-*m*-cresol phosphate (DCP) [1]. Much more often used method, is introduction of long side chains which improve solubility of polymer [15,36–41]. Thin films of solubilised polymers may be deposited from solution, e.g. by spin-on method. Each of these approaches have an impact on optical properties of resulting polyazomethine thin film. For example, introduction of solubilising octyloxy side chains into poly(1,4-phenylene-methylene-nitrilo-1,4-phenylene-nitrilomethylidene) structure not only enable polymer dissolution, but also induce better conjugation of the polyazomethine [42].

The aim of this study is to show the impacts of: (i) chemical structure modification (introduction and elongation of solubilising alkyloxy side chain and) (ii) thin film deposition technique (spin-on and CVD methods) on the optical properties of resulting thin films. Additionally combined influence of these two effects is presented. The study has been conducted on three azomethine structures, from which, to the best of our knowledge, two have never been reported before. Each structure has been obtained through a chemical synthesis and by a CVD method separately. Additionally, the study was supported by investigations of

* Corresponding author.

E-mail address: pnitschke@cmpw-pan.edu.pl (P. Nitschke).

model compounds. Obtained compounds have been characterised with proton nuclear magnetic resonance spectroscopy (^1H NMR), Fourier transform infrared spectroscopy (FTIR), wide angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), size-exclusion chromatography (SEC), thermogravimetric analysis (TGA), and by the spectroscopic ellipsometry. Apart from that, obtained thin films' surfaces have been investigated by the atomic force microscope (AFM). In our studies however, we mostly focused on the ultraviolet-visible-near infrared spectroscopy (UV-Vis-NIR) measurements. Since thin films obtained by CVD method were soluble, all structures were investigated in form of both: thin film and solution. Comparison of the optical absorption spectra of different structures shows the influence of introduction and elongation of alkyloxy side chain, while the comparison of spectra of thin films obtained by spin-on method with analogues obtained by CVD method shows the role of the route employed toward polymer thin film deposition. Presented results may be important during designing new materials and their synthesis routes for optoelectronic devices.

2. Experimental

Chemical structures of obtained polyazomethines and employed codes of investigated compounds are shown in the Chart below (Chart 1).

2.1. Materials

2,5-bis(octyloxy)terephthalaldehyde (BOO) (98%), 2,5-bis(methoxy)-terephthalaldehyde (BMO) (97%), Terephthalaldehyde (TPA) (98%), and trifluoroacetic acid (TFA) (99%) were purchased from Sigma-Aldrich and used as received. 2,5-diamino-thiophene-3,4-dicarboxylic acid diethyl ester (DAT) was synthesised according to literature [43]. The solvents: toluene, methanol and chloroform were purchased from Avantor Performance Materials, and used as received.

2.2. Synthesis of polymers and model compounds

Polyazomethines S-1, S-2 and S-3 were prepared by solution polycondensation of equimolar amount of DAT with adequate dialdehydes in toluene catalysed with TFA. Reaction mixtures were stirred at 100 °C under nitrogen atmosphere for seven days. Polymers were precipitated in methanol, filtered and washed thoroughly with pure methanol. A polymer powder was then cleaned by an extraction with refluxing

methanol in a Soxhlet apparatus for seven days and then dried at 120 °C for two hours.

Model compounds M-1, M-2 and M-3 were prepared by solution condensation of two equivalents of DAT with one equivalent of adequate dialdehyde in chloroform without catalyst, at room temperature. Reaction mixtures were stirred at room temperature for three days. After that time spontaneous precipitation of compounds has been noted. Precipitants were filtered and washed with methanol and then dried at 60 °C for a day.

2.2.1. Polymer structure 1 (S-1)

Yield: 86.6%
 UV-Vis-NIR (λ_{max}) (CHCl_3) 262, 302, 454 and 482 nm
 UV-Vis-NIR (λ_{max}) (spin-coated thin film) 482 and 520 nm
 FTIR (KBr) (cm^{-1}) 3398, 3310, 3272 (N–H end group), 3068 (C–H phenyl), 2964, 2930, 2904, 2864 (C–H aliphatic), 1738, 1718 (C=O aromatic ester), 1686 (C=N imine), 1596 (C=C thiophene), 1536, 1480 (C=C phenyl), 1426 (C–N imine), 1246 (C–O ester).
 ^1H NMR ($\text{CHCl}_3\text{-d}$) (δ ppm), 10.05 (s, 0.32H, –CHO; end group), 7.97 (s, 1H, CH=N), 7.78 (s, 1.98H, Ar–H), 6.4 (s, 4H, –NH₂; end group), 4.45–4.28 (m, 6.7H, O–CH₂), 1.46–1.34 (m, 10.4H, –CH₃)

2.2.2. Model structure 1 (M-1)

Yield: 69.5%
 UV-Vis-NIR (λ_{max}) (CHCl_3) 262, 306, 453.5 and 482 nm.
 UV-Vis-NIR (λ_{max}) (spin-coated thin film) 283, 482 and 520 nm.
 FTIR (cm^{-1}) 3397, 3310, 3271 (N–H end group), 3071 (C–H phenyl), 2978, 2934, 3903, 2865 (C–H aliphatic), 1740, 1719 (C=O aromatic ester), 1686 (C=N imine), 1596 (C=C thiophene), 1535, 1480 (C=C phenyl), 1426 (C–N imine), 1245 (C–O ester)
 ^1H NMR ($\text{CHCl}_3\text{-d}$) (δ ppm), 10.05 (s, 0.05H, –CHO; end groups from dimers), 7.93 (s, 1H, –CH=N–), 7.76 (s, 2.09H, Ar–H), 6.39 (s, 2.12H, –NH₂; end groups), 4.45 (q, 2.29H, –O–CH_{2a}–), 4.28 (q, 2.31H, –O–CH_{2b}–), 1.46 (t, 3.39H, –CH_{3a}), 1.34 (t, 3.43H, –CH_{3b})

2.2.3. Polymer structure 2 (S-2)

Yield: 70.2%
 UV-Vis-NIR (λ_{max}) (CHCl_3) 268, 312, 480 and 512 nm.
 UV-Vis-NIR (λ_{max}) (spin-coated thin film) 496 and 530 nm.
 FTIR (KBr) (cm^{-1}) 3308, 3250 (N–H end group), 3071 (C–H phenyl), 2979, 2958, 2937, 2903, 2867, 2832 (C–H aliphatic), 1715 (C=O aromatic ester), 1662 (C=N imine), 1588 (C=C thiophene), 1537, 1487 (C=C phenyl), 1291 (C–O ether), 1253 (C–O ester)

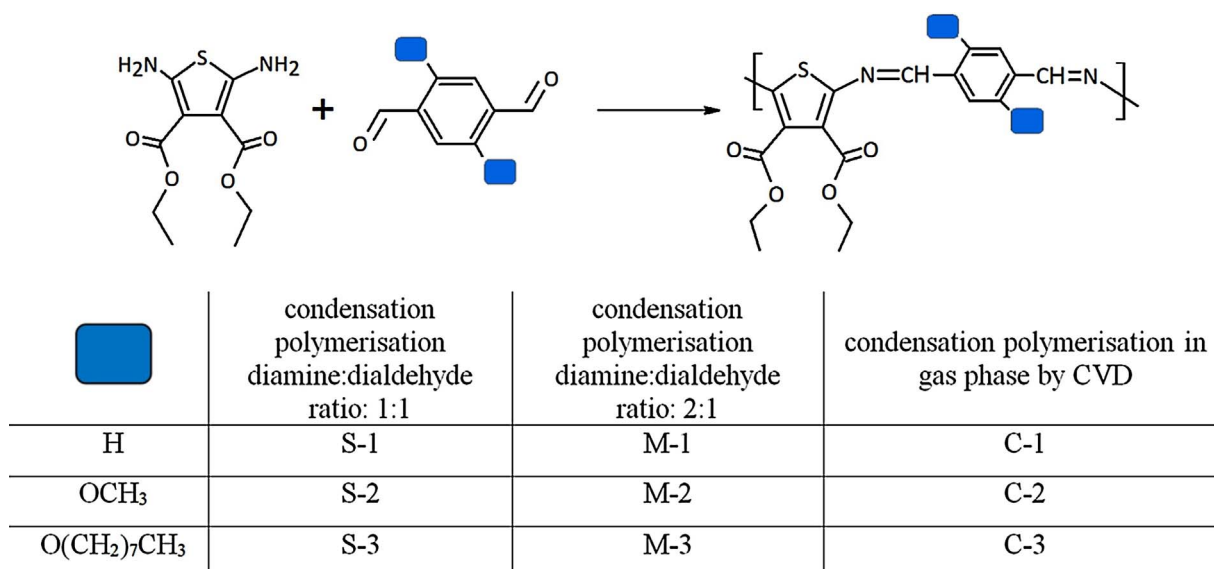


Chart 1. Chemical structures of investigated polyazomethines and their codes employed in the text.

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