



Self-assembly of nanostructured polymetallaynes

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ARTICLE INFO

Article history:

Received 21 January 2008

Received in revised form 7 May 2008

Accepted 11 May 2008

Available online 21 May 2008

Keywords:

Polymetallaynes

Nanostructured polymers

Nanofibers

ABSTRACT

Organometallic conjugated polymers containing transition metal centers in the main chain (polymetallaynes), with general formula $-[M-(PBU_3)_2-C\equiv C-X-C\equiv C-]_n-$ with $M = Pt(II)$ and $Pd(II)$, $X =$ organic conjugated spacer, namely poly[1,1'-bis(ethynyl)-4,4'-biphenyl-(bis-tributylphosphine)Pd(II)] (Pd-DEBP), poly[1,1'-bis(ethynyl)-4,4'-biphenyl-(bis-tributylphosphine)Pt(II)] (Pt-DEBP) and poly-[1,4-bis(ethynyl)-2,5-dihexadecyloxybenzene-bis(triphenylphosphine)platinum(II)] (Pt-BOB) were synthesized and fully characterized. The polymeric compounds were cast deposited onto glass substrates and their morphologies studied by means of SEM (Scanning Electron Microscopy) and EF-TEM (Energy Filtered-Transmission Electron Microscopy). The formation of nanostructured fibrils with diameters in the range 100–300 nm was revealed by SEM. EF-TEM images showed that the fibers are made of hollow nanotubes, randomly oriented, with external diameter of about 6–7 nm.

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1. Introduction

One-dimensional nano-sized polymeric materials, prepared by chemical or physical methods, have been investigated extensively [1–3] and their main features related to the properties of both the organic and the inorganic materials are reviewed [4].

Conducting polymeric nano-structures such as polyaniline, polypyrrole and polythiophene have been obtained by several strategies, including template synthesis, interfacial polymerization, self-assembly and stepwise electrochemical deposition [5].

Among these materials, conjugated polymers containing metal centers represent a class that possesses interesting optical and electronic properties. Organometallic polymers with high content of ethynyl bridging π -conjugated organic spacers in rigid-rod structure (polymetallaynes) have been synthesized and characterized [6]. Other molecular structures could be built by changing the configuration of the precursor complex. For example, self-assembled metallomacrocycles are reported with a variety of symmetric shapes, *i.e.* triangles, squares, and hexagons [7]. These shapes usually develop when *cis*-blocked square-planar Pt(II) and Pd(II) complexes are used.

These materials allow modeling their physical properties following a building block approach, *i.e.* changing the transition metal

center, the geometry around the metal, the organic spacer, the distance and the angles between metal centers [8]. It is expected that they may form molecular architectures at nanometric scale with relevant implications for technological applications such as molecular sensing, optoelectronics or catalysis [9]. In fact, the construction of precise shaped and sized macromolecules is strictly correlated to peculiar properties and efficiency in different applications [10].

The production of nano/microscaled fibers of polymeric materials is important because of their potentials in many fields of science and technology, such as tissue engineering, optoelectronics and drug delivery [11]. Two main techniques, electrospinning and porous templates, are reported for obtaining nano-tubular structures, for example bio-nanowebs and mesoporous carbon nanowires. The linear conjugated molecular structure of our polymetallaynes is expected to allow production of photo or electro-active nanostructures with an intimate control of the reactive properties. In this context, the production of nano-sized fibrils by simple self-assembly, as in the case of amphiphilic polymers [12] and polyelectrolytes [13], could be groundbreaking.

In this paper we report on polymetallaynes prepared at a nanoscale size, forming unforeseen hollow tubes with a diameter of a few nanometers and up to microns long. The synthesis of these linear rigid-rod-like structures is based on the coupling of *trans* metal dihalides with conjugated dialkynes, yielding polymers with partially delocalized π electrons, which result from the interaction of the metal d orbitals with π^* orbitals of the alkyne [14].

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2. Experimental

2.1. Material and methods

All reactions were performed under an inert argon atmosphere. Solvents were dried on Na_2SO_4 before use. All chemicals, unless otherwise stated, were obtained from commercial sources and used as received. The compound 4,4'-diethynyl-biphenyl (DEBP) was prepared according to literature methods [15]. Platinum and palladium complexes $[\text{MCl}_2(\text{PBU}_3)_2]$, with $\text{M} = \text{Pt}$ or Pd , i.e. *cis*-[dichlorobis(tributylphosphine)platinum(II)], *trans*-[dichlorobis(tributylphosphine)platinum(II)] and *trans*-[dichlorobis(tributylphosphine)palladium(II)] were prepared by reported methods [16]. Preparative thin-layer chromatography (TLC) separation was performed on 0.7 mm silica plates (Merck Kieselgel 60 GF254) and chromatographic separations were obtained with 70–230 mesh alumina (Merck), by using *n*-hexane/dichloromethane mixtures.

The organometallic polymers Pt-DEBP, Pd-DEBP, i.e., poly-[1,1'-bis(ethynyl)-4,4'-biphenyl(bis-tributylphosphine)Pt(II)] and poly-[1,1'-bis(ethynyl)-4,4'-biphenyl(bis-tributylphosphine)Pd(II)] were synthesized from equimolar amounts of dichloride square-planar complexes *trans*- $[\text{Pd}(\text{PBU}_3)_2\text{Cl}_2]$ or *trans*- $[\text{Pt}(\text{PBU}_3)_2\text{Cl}_2]$ in the presence of monomer 1,1'-bis(ethynyl)-4,4'-biphenyl (DEBP) in NH_4Et_2 as solvent and base. For a typical dehydrohalogenation synthesis, 0.8 mmol of DEBP and an equimolar amount of the Pt(II) or Pd(II) complexes $[\text{M}(\text{PBU}_3)_2\text{Cl}_2]$ were added in the reaction flask in the presence of argon-bubbled diethylamine as solvent and base (30 ml). The reactions were allowed to react for different times at 60 °C. Ammonium salts were then removed by filtration and the residual dark brown solution reduced in volume with a rotating evaporator.

Poly-[1,4-bis(ethynyl)-2,5-dihexadecyloxybenzene-bis(triphenylphosphine)platinum(II)] (Pt-BOB) was synthesized by following the *Extended One Pot*, (EOP) synthetic procedure [17]. To 900 mg of 1,4-diiodo-2,5-di(butoxy)benzene (1.91 mmol), dissolved in THF, 1.196 g (3.80 mmol) of tributylethynyltin were added under Ar, followed by the catalyst $[\text{Pd}(\text{PPh}_3)_4]$ (88 mg, 0.07 mmol). After stirring at 70 °C for 18 h, the reaction mixture was cooled at 0 °C and LDA 2 M added (2.47 ml, 5.0 mmol). *Cis*-bis(triphenylphosphine)platinum(II) (1.425 g, 1.88 mmol) was then introduced into the vessel and the mixture warmed up at 70 °C for 24 h. At this point the solution was left to cool at room temperature and the volume reduced in vacuum. Addition of pentane allowed the separation of red oil (1.36 g, 73% yield).

2.2. Characterization of the reaction products

2.2.1. Pt-DEBP

IR (film, cm^{-1}) ν ($\text{C}\equiv\text{C}$): 2094, 2932, 2870, 1602, 1485, 1463, 1373, 1213, 1093, 971, 904, 720, 401, 393; UV (CHCl_3): 372.2 nm; ^1H NMR (CDCl_3 ppm): 7.44 (d, 4H, Ar-H), 7.29 (d, 4H, Ar-H), 2.15 (m, 12H, P- CH_2 -), 1.62 (m, 12H, P- CH_2 - CH_2 -), 1.45 (q, 12H, P- CH_2 - CH_2 - CH_2 -), 0.93 (t, 18H, - CH_3 , $J = 9.00$ Hz); ^{31}P NMR (CDCl_3 , ppm, ($J^{195}\text{Pt}-^{31}\text{P}$) Hz): 3.72 (2358), 7.52 (2371); Elemental analysis (%), found (calculated for the repeating unit $\text{C}_{40}\text{H}_{62}\text{P}_2\text{Pt}$): C = 59.20 (60.06); H = 8.09 (7.81).

2.2.2. Pd-DEBP

IR (film, cm^{-1}) ν ($\text{C}\equiv\text{C}$): 2096, 2932, 2872, 1601, 1488, 1463, 1378, 1210, 1092, 903, 721, 443, 396; UV (CHCl_3): 352.6 nm; ^1H NMR (CDCl_3 ppm): 7.44 (d, 4H, Ar-H), 7.28 (d, 4H, Ar-H), 2.02 (m, 12H, P- CH_2 -), 1.58 (m, 12H, P- CH_2 - CH_2 -), 1.43 (q, 12H, P- CH_2 - CH_2 - CH_2 -), 0.92 (t, 18H, - CH_3 , $J = 9.00$ Hz); ^{31}P NMR (CDCl_3 , ppm): 11.29, 10.47; Elemental analysis (%), found (calculated for the repeating unit $\text{C}_{40}\text{H}_{62}\text{P}_2\text{Pd}$): C = 65.56 (67.54); H = 8.87 (8.79).

2.2.3. Pt-BOB

IR(film, cm^{-1}) ν ($\text{C}\equiv\text{C}$): 2104, ν (C-Sn): 525, 533; 394, 280; UV (CHCl_3): 396.0 nm; ^1H NMR (CDCl_3 ppm): 7.72 (m, P-Ar-H), 7.35 (m, P-Ar-H), 6.56 (Ar-H), 3.75 (t, O- CH_2 -), 2.09, 1.59 (m, - CH_2 -), 1.35 (m, - CH_2 -), 0.90 (m, - CH_3); ^{31}P NMR (CDCl_3 , ppm, ($J^{195}\text{Pt}-^{31}\text{P}$) Hz): 18.07 (2654.0), 17.67 (2610.0), (intensity ratio = 1:1); Elemental analysis (%), found (calculated for the tetranuclear structure $\text{C}_{258}\text{H}_{274}\text{O}_{10}\text{P}_8\text{Pt}_4\text{Sn}_2$): C = 63.95 (64.55), H = 5.74 (5.75).

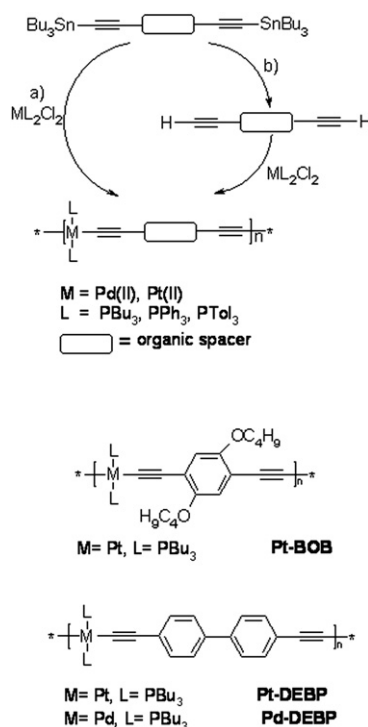
2.3. Instrumentation

FTIR spectra were recorded as nujol mulls or as films deposited from CHCl_3 solutions by using CsI cells, on Bruker Vertex 70 Fourier Transform spectrometer. ^1H , ^{31}P NMR spectra were recorded in CDCl_3 on a Bruker AC 300P spectrometer at 300 and 121 MHz, respectively; the chemical shifts (ppm) were referenced to TMS for ^1H NMR assigning the residual ^1H impurity signal in the solvent at 7.24 ppm (CDCl_3). ^{31}P NMR chemical shifts are relative to H_3PO_4 (85%). UV-vis spectra were recorded in CHCl_3 solutions at room temperature on a Varian Cary 100 instrument.

Light scattering measurements were performed at the temperature of 20 °C, using a home made photogoniometer equipped with a logarithmic correlator (Brookhaven, mod. BI900 AT) and the light source was a 10 mW He-Ne laser (k 1/4 632:8 nm).

Scanning Electron Microscopy (SEM) measurements were made on samples deposited by slow evaporation from toluene solutions (1 mg/ml) on glass substrates, freshly cleaned by immersion (30 min) in KOH/EtOH solution and accurately rinsed with H_2O , EtOH, CHCl_3 and toluene. The SEM instrument was a Leo 1450 VP equipped with a back-scattered electrons detector, of resolution 3.5 nm.

Energy Filtered-Transmission Electron Microscopy (EF-TEM) measurements were carried out. A droplet of the aqueous suspension, containing fibers, was deposited onto 400 mesh copper grids for electron microscopy, covered with a very thin amorphous



Scheme 1. Synthetic strategies for polymetallaynes and chemical structures for Pt-DEBP, Pd-DEBP and Pt-BOB.

carbon film (about 20 nm) and the excess of liquid was removed by placing the grid on filter paper. The samples were studied in a Zeiss 902 Transmission Electron Microscope, operating at 80 kV, equipped with an Electron Energy Loss Filter. In order to enhance contrast and resolution, the microscope was used in the Electron Spectroscopy Imaging (ESI) mode filtering at $\Delta E = 0$ eV. The image acquisition was performed by a digital CCD camera model HSC2, 1k for 1 kpixels, (PROSCAN GMBH, Germany), thermostated by a Peltier cooler model WKL 230 (LAUDA GMBH, Germany). Image analysis and quantification was performed by a digital image analyzer analySIS 3.0 (SIS GMBH, Germany). This software allows to enhance contrast and sharpness of the acquired images and to perform morphological quantification and statistics. The dimensional measurements were performed after a careful magnification calibration of the whole imaging system based on reference standards (cross-grating and catalase crystal).

Computer models of hollow nanotubes consisting of an even number m of multinuclear Pt dialkynyl bridged oligomers were calculated by means of simple geometric transformations of the atomic coordinates of a single molecule. The molecule is first reoriented such that the first Pt atom is positioned at the origin, the

Pt–Pt axis aligns with the z -axis, and the diphenyl mean plane aligns with the yz -plane. It is then translated by $w/2 + v/(2 \tan(\pi/m))$ along the x -axis and copied m times. The i^{th} copy is rotated by $2\pi i/m$ around the z -axis and every second molecule is translated by $u/2$ along the z -axis. The dimensions u , v , and w were derived from the crystal structure of the binuclear Pt dialkynyl bridged complex (complex 1 in Ref. [18]): $u = 16.343$ Å (the distance between the two Pt atoms of a molecule), $v = 5.153$ Å (the distance between the Pt–Pt axes of two parallel molecules in a layer of molecules), and $w = 10.864$ Å (the shortest distance between the diphenyl planes of two molecules in separate layers of molecules). No free energy calculation or optimizations were performed.

3. Results and discussion

Polymetallaynes Pt-DEBP, Pd-DEBP and Pt-BOB were synthesized from square-planar bis-phosphine-dichloride-platinum(II) or palladium (II) complexes. Methods for synthesizing these polymetallaynes are based mainly on two convergent strategies (Scheme 1).

Stannyl protected dialkynes were used as precursor monomers for the reaction between electrophiles and organotin reagents in the presence of palladium [19], according to a modified version of the Stille method [20] (Scheme 1, path a). Alternatively a dehydrohalogenation reaction was adopted [21] when free dialkynes were accessible (Scheme 1, path b). The use and the choice of different synthetic pathways allowed the formation of polymers and oligomers of controlled length. All the above mentioned macromolecules have a linear “rod-like” molecular structure.

The dehydrohalogenation reaction (Scheme 1, path b) has been in depth investigated for the polymerization of diethynyl-biphenyl

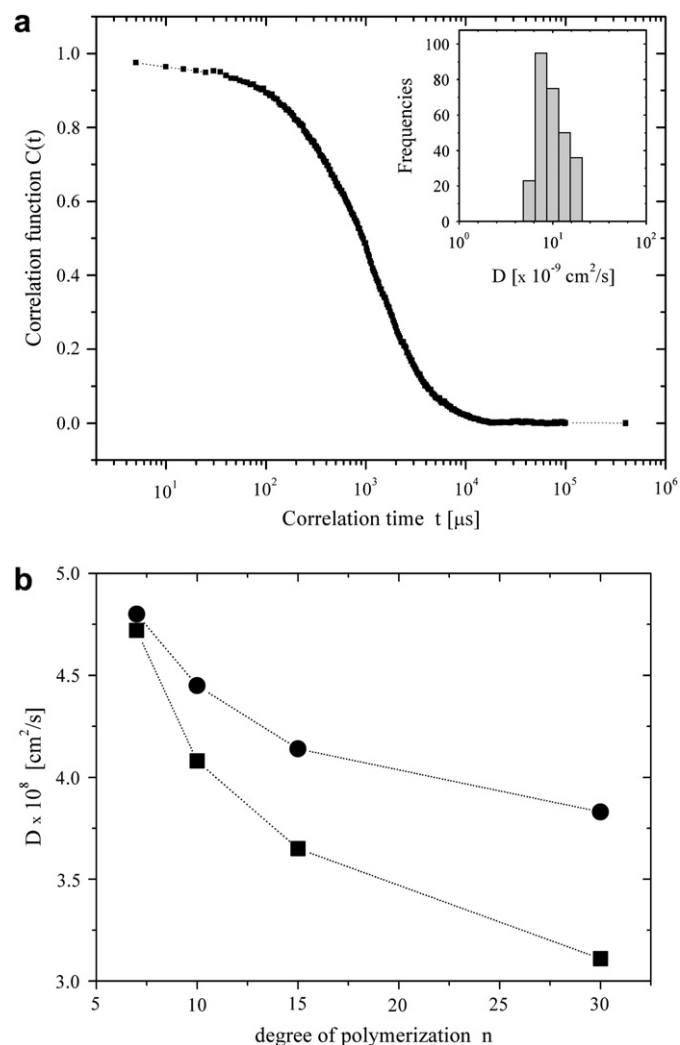


Fig. 1. (a) Intensity–intensity correlation function of the scattered light of Pt-DEBP in toluene solution as a function of the correlation time. The inset shows the distribution of the diffusion coefficients derived from the CONTIN analysis of the correlation function; (b) the average diffusion coefficients of Pt-DEBP as a function of the number of repeating units, for two different solvents: (circles): toluene; (squares): trichloromethane.

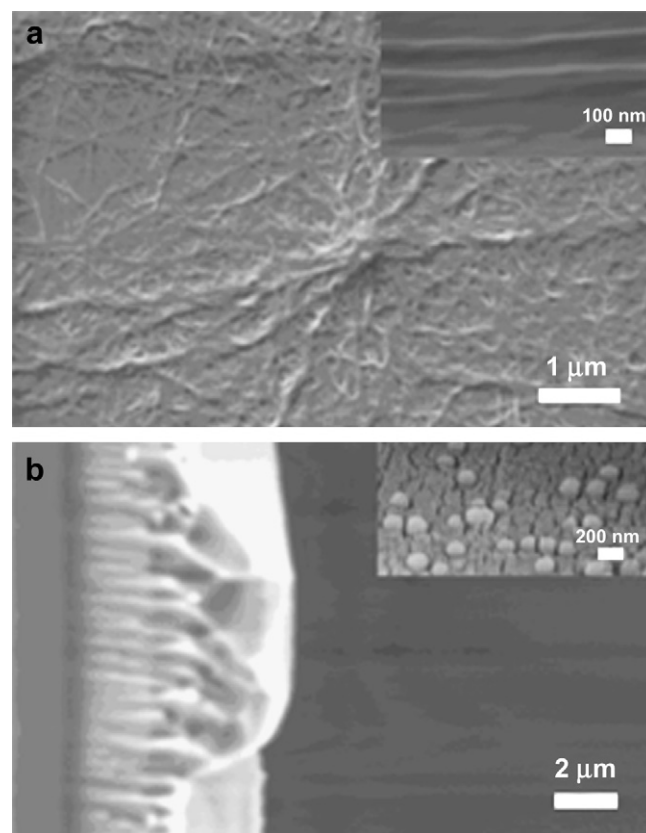


Fig. 2. (a) SEM images of Pt-DEBP, cast deposited on glass from toluene solution; inset: a detail; (b) SEM images Pt-BOB, cross-section; inset: grain surface.

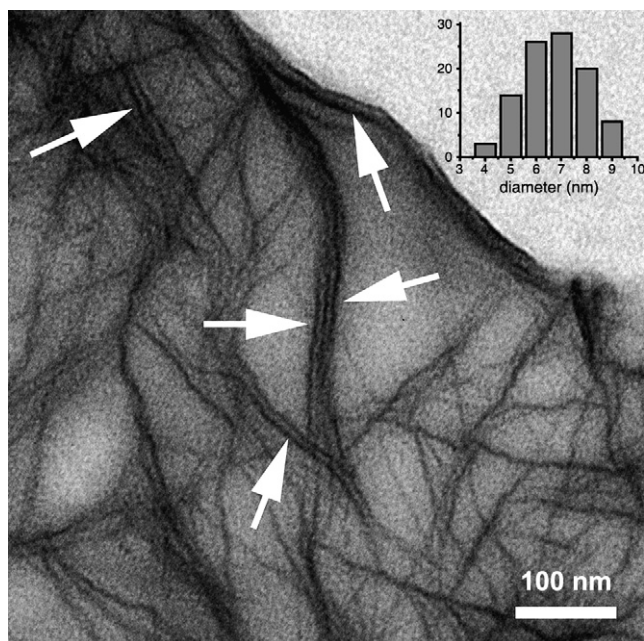


Fig. 3. TEM images of Pt-DEBP nanotubes.

(DEBP) monomer with bis-phosphine Pt and Pd dichlorides, leading to Pt-DEBP and Pd-DEBP polymers [22]. Attention was paid to the control of the synthetic conditions and to their influence on the chain growth. In addition, the influence of the configuration of the precursor complexes, *i.e.* *cis* and *trans* Pt(II) isomers, on the number of the repeating units was considered. The length of the oligomers containing DEBP spacer was in the range from 2 to 20 repeating units, measured by ^{31}P NMR spectroscopy combined with XPS and GPC data.

The hydrodynamic behavior of Pt-DEBP polymers in two different organic solvents (toluene and trichloromethane) has been investigated by means of dynamic light scattering (Fig. 1). A typical intensity–intensity autocorrelation function of the scattered light is shown in Fig. 1a, together with the distribution of the diffusion coefficient D derived from the deconvolution of the correlation function carried out by means of the CONTIN algorithm. Fig. 1b, shows the average diffusion coefficients of the Pt-DEBP polymers as a function of the number of the repeating units, for the two solvents investigated. The results show that polymer chain conformation is influenced by the solvent, being more compact in toluene than in trichloromethane.

In order to quantify the hydrodynamic hindrance of the polymer in solution, the hydrodynamic radii of the diffusing polymer chains have been calculated from the diffusion coefficients D using the Stokes–Einstein relationship. The “equivalent” hydrodynamic radius R_{H} increases from about 80 to 125 nm for the polymer in trichloromethane and from about 80 to 100 nm for the polymer in

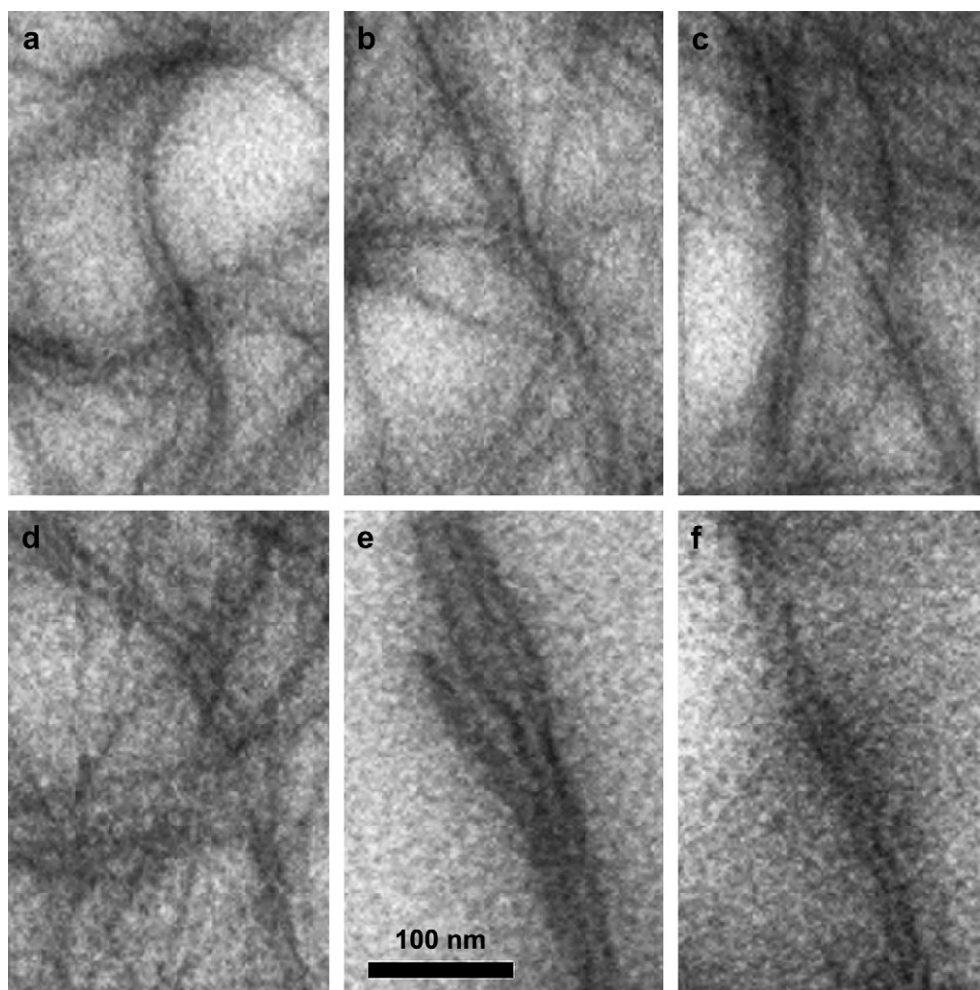


Fig. 4. TEM images of Pt-DEBP nanotubes, details.

toluene, as the number of the repeating units is increased from 7 to 35.

The molecular orientation of the polymers after deposition on solid substrates is a prerequisite for their self-assembly into larger structures and important for the improvement of the performance of these materials. This was previously studied by means of NEXAFS (Near Edge X-ray Absorption Fine Structure) and EXAFS spectroscopy [23]. The molecular orientation of polymetallaynes leads to the assembly of the macromolecules into fibers, which enhance the sensitivity to chemical vapors of SAW (Surface Acoustic Wave) sensors [24].

The surface morphologies of Pt-DEBP and Pd-DEBP were further investigated by means of SEM (Scanning Electron Microscopy). When solutions of these materials were cast on glass substrates, fibrils were formed depending on the evaporation rate of the solvent (toluene was the more suitable). Ropes were found randomly oriented on the solid surface, with diameters ranging from 100 to 300 nm, made of smaller fibers with less than 100 nm in diameter (Fig. 2a).

The influence of the metal-bound organic spacer on surface morphology and polymer aggregation was studied. Significant differences were observed: in the case of a substituted diethynylbenzene (BOB) linked to Pt(II) centers in the polymer backbone, *i.e.* Pt-BOB (Fig. 2b). The chains self-organize into columnar nanosize structures, growing nearly perpendicular to the substrate, with 150 nm diameter and a spatial separation of about 200 nm. At high resolution, the film surfaces show a nanoporous structure with grain shapes of about 100 nm diameter (Fig. 2b, inset). These morphologies are related to the response to water vapors and hydrogen of chemical sensors based on membranes made by related polymers, probably due to the enhanced surface area available for the polymer/molecule interaction, as previously reported for a similar structure [25].

Energy Filtered-Transmission Electron Microscopy (EF-TEM) was used to further investigate the structure of fibrils observed by SEM. Pt-DEBP polymer solution was cast on a Petri vessel and the solvent (toluene) slowly evaporated at room temperature in controlled environment. Polymer chains self-organized into fibrils and ropes, which were dispersed in distilled water and imaged by

EF-TEM. At high magnification a homogeneous carpet made of long and interconnected fibers (up to few microns) is visible (Figs. 3 and 4). Solid and double-lined (see arrows in Fig. 3) structures can be observed, often placed side by side. We suppose that the double-lined structures represent the outer walls of hollow nanotubes. First, double-lined structures are typically observed by TEM when imaging tubular structures [26]. Second, the samples were not stained and the contrast arises from the electron scattering due to the heavy Pt atoms. Tube walls oriented along the electron beam have a higher Pt thickness and scatter fast electrons more efficiently than other parts, resulting in a darker feature in the TEM image. Conversely, the internal, empty axis appears brighter. We conclude that often the fibrils are made of hollow molecular tubes, randomly oriented, with external diameter of about 6–7 nm (Fig. 3 inset). The solid structures might be composed of tightly packed, almost parallel polymer chains, producing rigid-rod molecular structures.

Not all tubes are well formed, however, those that are formed can self-assemble and give rise to filaments and fibers.

Molecular models of hollow nanotubes were calculated based on the crystallographic data of a model complex [18] in order to illustrate possible arrangements of the polymer chains (Fig. 5).

The models show the geometric feasibility of forming hollow nanotubes with diameters observed in TEM images (Fig. 3) out of 24–36 parallel polymer chains (only even numbers are allowed) arranged in circular shapes.

4. Conclusions

In conclusion, organometallic polymers and oligomers containing transition metal centers in the main conjugated chain (polymetallaynes) upon deposition of the solution on a solid substrate form a more or less compact aggregate where the single chains organize themselves in nanotubes with a further self-assembling towards a meso-scale fibril aggregate, as shown by SEM and TEM. The nanosize is achieved by a simple self-organization of hollow nanotubes (diameters in the range 5–10 nm) in fibrils several microns long.

Acknowledgements

The authors gratefully acknowledge the financial support of MIUR (Italy) to this research work.

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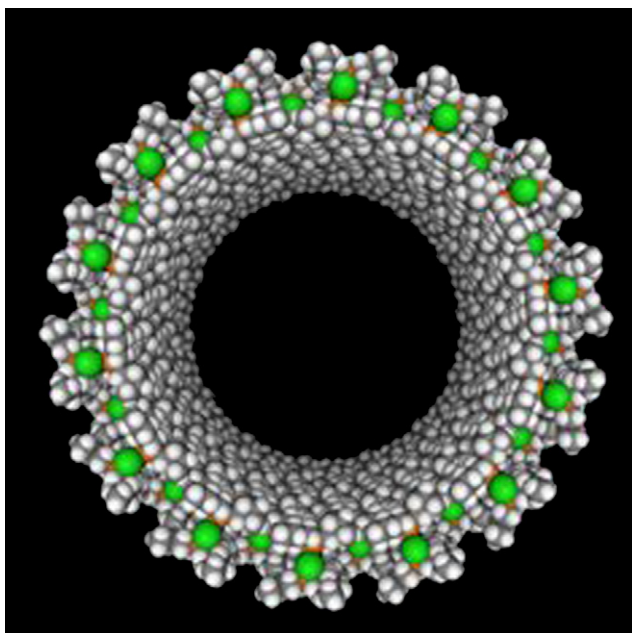


Fig. 5. Computer model of Pt-DEBP hollow nanotube made of 28 parallel polymer molecules. The diameter of ~6.8 nm matches TEM results (Fig. 3).

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