

# Hard template synthesis of conducting polymers: a route to achieve nanostructures

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**Abstract** The article reviews the application of a hard template approach in the formation of conducting polymers nanostructures. The method involves the synthesis of a polymer within the pores or channels of a template. The influence of synthesis conditions on fundamental features of nanostructured polypyrrole, polyaniline, and their derivatives is discussed.

**Keywords** Polyaniline · Polypyrrole · Nanostructures · Template synthesis

## Introduction

This publication is dedicated to Professor O. A. Petrii, a distinguished Russian electrochemist, on his 70th birthday anniversary. Professor O. A. Petrii is interested and involved in many aspects of contemporary electrochemistry, including nanoelectrochemistry [1].

In the last three decades, conducting polymers (CPs) have received a considerable attention because of their interesting electronic and physical properties, chemical stability, and potential technological applications [2–4]. CPs synthesized in the form of one-dimensional nanostructures such as nanotubes, nanofibers, and nanowires are of particular interest, as their properties significantly

differ from the properties of the corresponding macroscopic materials. Some of these special, physical, and chemical properties will render CPs useful for new applications in nanodevices [5]. It is acknowledged that typical nanomaterials or nanostructures have dimensions ranging from 1 to 100 nm. However, in the case of CPs and some biological objects, this range is widened to about 500 nm. Many different techniques and strategies for formation of CP nanostructures have been developed and employed—ranging from template synthesis to no-template synthesis. They have been described and discussed in some earlier and current brief reviews [6–14]. According to Zhang et al. [14], the template synthesis may be divided into “hard template” synthesis and “soft template” synthesis, which in literature is often called template-free or self-assembly synthesis [15–17].

The hard template approach, proposed by Martin [6, 7, 18], involves a synthesis of CP within the pores or channels of membranes. In general, two types of membranes were used by Martin’s group: track-etch polycarbonate (PC) or polyester (PE) membranes and anodic aluminum oxide (AAO) membranes.

However, also other solid porous materials, such as zeolites [19], silica-based mesoporous molecular sieves [20], oxides [21, 22], graphite composites [23, 24], polyoxometallates [25], and previously synthesized nanostructures (for example, carbon nanotubes and Ag, Au, or Ni nanoparticles) [26–29] can be used in hard template synthesis of CP nanostructures.

Dimensions as well as geometry of the CP nanostructures can be controlled by selecting an appropriate template. The synthesized nanostructures can be kept inside the pores of the template or they can be released from the template. In the first method, an array within the template or a composite material is formed, whereas as a result of the

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Dedicated to the 70th birthday of Professor Oleg Petrii.

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second method, free nanostructures are obtained, either in the solution or on a surface of a different substrate.

The soft template synthesis requires the presence of the structure-directing molecules, for example surfactants [12, 17, 30–32], deoxyribonucleic acid [33, 34], lipid tubules [35], liquid crystalline [36], adsorbed thiolates [37], and so on.

Both of the above-described approaches exhibit some advantages and disadvantages. By applying the hard template method, we are able to prepare highly oriented and ordered one-dimensional nanostructures of CP: nanotubules, nanowires, and nanofibers. However, after the polymer nanostructures are formed, the template material should be etched away. During this postsynthesis process, the soft polymeric structures may be damaged or obtained in the form of aggregates. The soft template method is simpler and less expensive in comparison to the hard template method because it eliminates the use of the solid template and postsynthesis etching procedure. However, in both of these approaches, there is a crucial point while working with the free nanostructures, one must employ some pick-and-place technique to capture the nanostructures and to position them at the point of use. There are many techniques, which can be applied for assembly formation of nanostructure arrays for integrated systems. Examples of such techniques include atomic force microscope manipulation of nanostructures onto patterned electrodes, electric field-induced orientation, Langmuir–Blodgett alignment, and the grow-in-place method [38–42]. In addition to the template approach, the CP nanostructures can be formed by no-template techniques, such as radiolytic, sonochemical, electrochemical techniques, rapid mixing reactions, and interfacial polymerization. These methods as well as the soft template approach are briefly discussed in the review of Zang and Wang [14], wherein synthesis and applications of nano-structured polyaniline (PAni) are described.

The present article aims to provide a brief overview of the application of the hard template approach in formation of nanostructured polypyrrole (PPy), polythiophene (PTh), PAni, and their derivatives. The influence of synthesis conditions on fundamental features of these nanostructures is also discussed herein. It should be mentioned that because of a significant number of articles on this topic published every month, this review might have omitted some of them.

## Methods of synthesis

In general, the bulk CPs may be obtained by using chemical or electrochemical synthesis. Both of these methods have been applied for formation of nanostructured CPs.

The chemical template synthesis can be accomplished in a simple way by immersing the membrane in a solution

containing the desired monomer and subsequent addition of the oxidizing agent. Such procedure was applied in obtaining of PPy [43–46], PAni, and poly(1,8-diaminonaphthalene) (P(1,8-DAN)) [47–52] nanostructures.

In other procedure, employed for the formation of PPy [53–56], poly(3-methylthiophene) (PMTh) [53], and PAni [57], a template membrane separates two cells, one containing the solution of a monomer and the other—an oxidizing agent. In this case, the monomer and the oxidant diffuse toward each other through the pores of the membrane and react within the pores to yield the polymer. In addition to the “wet” methods described above, the monomers can be absorbed from vapor phase into the membrane channels of the template and further polymerized chemically by the oxidant in the vapor phase or in solution [58].

In electrochemical polymerization, the deposition process of CP within pores is accomplished by coating one surface of a membrane with a thin metal film, for example Pt or Au. This way, a working electrode on one side of the membrane is obtained. During the electropolymerization process, the pores are filled up beginning from the bottom (i.e., from the working electrode) to the uncovered, top surface of the membrane. By controlling the polymerization time, thin-walled tubules, thick-walled tubules, or fibrils can be formed. If the polymerization time is too long, a thin film is formed on the top of membrane. Electrochemical template deposition was widely used for formation of PPy [59–73], poly(3,4-ethylenedioxythiophene) (PEDOT) [64, 67, 70–72], PTh, PMTh [69, 72], PAni, P(1,8-DAN) [74–83], and poly(*o*-methoxyaniline) (PoMA) [78, 79]. In comparison to the chemical synthesis, the electropolymerization can be carried out in a more controllable way.

## Properties and synthesis conditions

The properties of the chemically synthesized PPy, PTh, PAni, and other polymer nanostructures depended on the reaction conditions, such as the membrane characteristics, the monomer concentration, the oxidant type, the monomer-to-oxidant ratio, the polymerization time, and the reaction temperature.

In the electrochemical synthesis, the properties of CP can be influenced not only by changing the chemical factors, including a monomer concentration and a type of doping ions, but also by controlling the potential, time, and charge of the polymerization process.

## Templates

Most of the studies in hard template synthesis have entailed the use of two types of nanoporous materials: particle track-

etched polymeric membranes (PTMs) and porous alumina membranes obtained by anodic oxidation of aluminum in acid solution. PTMs are available with a wide range of pores diameters (some as small as 10 nm) and pores densities ranging from  $10^5$  to  $10^9$  pores per  $\text{cm}^2$ . Whereas in the case of the alumina membranes, the pore densities may be as high as  $10^{11}$  pores per  $\text{cm}^2$ . Moreover, the structure of the polymeric and oxide membranes is different. Polymeric membranes, mostly PC or PE, contain randomly distributed cylindrical pores of uniform diameters [6, 7, 18, 84]. However, not all pores of the PTMs are perpendicular to the membrane surface. In many cases, the angle of the pores with respect to the surface normal can be as large as  $34^\circ$ , which results in the intersection of some pores within the membranes. The AAO membrane pores are also cylindrical with uniform diameters; however, they are arranged in a hexagonal array. Moreover, unlike in the PTMs, the pores have little or no tilt with respect to the surface normal, which results in the isolated pore structure [6, 7, 18, 56, 83]. Both the PTMs and AAOs are commercially available; however, in some publications, it has been demonstrated that the template membranes can be obtained directly in the laboratory. The group of Demoustier-Champagne [62, 64] has performed many of the investigations using the home-laboratory-formed PTMs. This approach has increased the control over the membrane structure [84]. Moreover, highly ordered CP nanostructures can be obtained by using AAO templates, i.e., the template, which is often formed electrochemically in the laboratories [51, 73, 77, 83].

The PC track-etched membranes (PC-PTM) and the AAO membranes were applied for both chemical and electrochemical synthesis of PPy (PC: [43–45, 53, 54, 60–63], AAO: [45, 46, 59, 67, 70, 71, 73]), PANi (PC: [47–49, 51, 57, 74, 80], AAO: [50, 51, 67, 71, 77, 83]), PTh, PMTh [53, 69, 72], PoMA [48, 78], and P(1,8-DAN) [52, 79]. Based on the reviewed publications, it can be concluded that track-etched polymer membranes are preferred in the chemical or electrochemical synthesis of the free CP nanostructures, while the AAO membranes are often used in electrochemical formation of nano-CP arrays. In our opinion, the postsynthesis-etching process, which is easier for PC membranes, is the main reason for different applications of PC-PTM and AAO membranes. To obtain free-standing CP nanostructures, the membranes should be dissolved. Generally, for dissolution of PC-PTMs, organic solvents such as dichloromethane and chloroform are used. In the case of AAO membranes, solutions of NaOH are applied. However, in both cases, the template-dissolving solvent can change the properties of nanostructures. It was found by Kim et al. [71] that such solvent like NaOH causes dedoping of CP and significant decrease in conductivity. The organic solvent cannot dedope CP;

however, it can swell up the nanostructures changing their diameters and morphology.

#### Morphology–template relationship

As it was mentioned above, the hard template synthesis is carried out by introducing the monomer into the pores of the template and subsequent chemical or electrochemical polymerization of monomer. Because of the template confinement, the size and shape of the obtained product should theoretically reflect the size and shape of the pores or channels of the template.

As it was demonstrated by the group of Martin [6, 7, 18, 43, 44, 47], when the PPy, PANi, and PMTh is synthesized within the pores of PC-PTMs chemically or electrochemically, the polymer nucleates and grows preferentially on the pore walls. Therefore, the polymeric tubules are formed, and their thickness and length depend on the synthesis conditions. By controlling the polymerization time, one can control the thickness of tubule walls [85]. The results obtained with PPy and PANi tubules indicated that the layer of polymer growing directly on the pore wall is highly ordered, reflecting the order of the polycarbonate chains of the membrane surrounding the pores. However, as the thickness of the tubule increases, the order within the polymer nanostructures decreases. Comparing the formation of PANi and PPy structures, it can be observed that the PANi tubules do not close up, even after a long polymerization time. In contrast, the PPy tubules, after long polymerization time fill in completely, forming fibers or wires. Martin et al. [6, 7, 18] suggested that the preferential nucleation on the pore wall results from two effects: a solvophobic effect and the electrostatic interaction between the anionic sites on the pore walls and polycationic forms of the forming polymer. In the same way, Xiong et al. [50] described the mechanism of formation of highly ordered PANi nanotubes in the AAO channels by chemical synthesis. Their results have also demonstrated that the diameter and length of PANi nanotubules reflect the pore size and thickness of the AAO template, respectively, and the arrangement of PANi nanotubules is very regular and uniform. However, such behavior is not observed in every case. Yang et al. [51], by comparing the morphology of PANi synthesized in AAO and in PC-PTM membranes, have shown that the membrane properties and pore size affect the order of PANi chains in the nanotubules. Duchet et al. [54] investigated the influence of pore size of the commercially available PC-PTM membranes on morphology of chemically synthesized PPy. They found that when the pore diameter exceeds 100 nm, the freed PPy tubules are rigid and form a brush-like structure, while for a diameter less than 100 nm, the obtained tubules are flexible. Further morphological analysis [54] has demonstrated that

the pores of the commercial membranes are not cylindrical, and they do not present a monodisperse distribution of the pore diameter. Consequently, the obtained nanotubules are not cylindrical but rather shaped like a cigar.

Szklarczyk et al. [78] investigated the electrochemical formation of PoMA in PC-PTM membranes with a variety of pore diameters. They found that the polymer grew simultaneously at the metal-covered, bottom surface of the membrane and the pore walls. This three-dimensional growth resulted in the formation of fibrils or end-capped nanotubes. The authors have suggested that this effect is caused by metal deposition inside the pores during evaporation of the metal layer on the surface of the membrane. They have also used the atomic force microscopy method to show that the membrane pores are not equally valuable for the nanostructure formation and that the diameter of nanostructures can be higher than the pore diameter of the membrane used as a template. This increase in the nanostructure diameter was observed earlier for PPy nanowires [86].

#### Morphology—chemical, electrochemical factors

Chemical polymerization of CP can be carried out with a variety of the chemical oxidants, such as ammonium peroxydisulfate (APS), ferric cations, permanganate, bichromate, and vanadate anions [10]. They are able to oxidize monomers yielding highly active intermediate species, cation radicals, thus initiating the polymerization process. Once formed, the intermediate species react with the monomer molecules or with themselves yielding oligomers and polymers. The properties of the final product depends on many factors, like the nature of the oxidant, the ratio of monomer to oxidant concentration, and the polymerization time, to mention just a few of them.

As an oxidant in the chemical formation of PPy, PTh, PMTh nanostructures, aqueous solutions of  $\text{FeCl}_3$  or acetonitrile solutions of  $\text{Fe}(\text{ClO}_4)_3$  and  $\text{FeCl}_3$  were used [45, 46, 53–56]. Concentrations of the oxidant and monomers were different, but in many cases, the concentration of oxidant was equal or higher than the monomer concentration. In chemical polymerization of PANi nanostructures, as an oxidant, an aqueous solutions of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , (APS) or  $\text{NaVO}_3$  were used [47–51, 57]. In many publications [47–49, 51], the maintained ratio of the monomer to oxidant concentration equaled 3. This value was determined as optimal during the chemical synthesis of the bulk three-dimensional PANi. To obtain conducting nanostructures, PANi synthesis was carried out in HCl or  $\text{HClO}_4$  solutions.

There are only a few works in which the chemical reaction conditions were modified to obtain more regular, more ordered, and more stable PPy and PANi nanostructures.

The group of Demoustier-Champagne [54] investigated the effect of the polymerization time and the reagent concentration on morphology of PPy nanostructures. It has been demonstrated that even extending polymerization time from 20 min to 16 h and increasing concentration of the monomer and  $\text{FeCl}_3$  up to 1 and 2 M, respectively, did not result in the formation of the PPy wires in pores of the PC-PTMs. The only observed difference between short and long polymerization times and between low and high reagent concentrations was the thickening of the polymer surface layer on the top of the membrane. This group has also studied [57] the influence of the oxidant nature ( $\text{NaVO}_3$ ,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ), the monomer/oxidant ratio, the polymerization time, and the addition of *p*-toluene sulfonic acid on PANi formation. They have shown that in contrary to Cepak and Martin [87], in the presence of  $\text{NaVO}_3$ , PANi grew nonuniformly leading to irregular and broken nanotubules. No changes in morphology were observed by varying the monomer/oxidant ratio from 3 to 10. The well-shaped PANi tubules were obtained when the oxidizing agent was changed to  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ . By investigating many parameters, they have also optimized conditions for formation of PANi tubules in the conductive state within the pores of various sizes. Tagowska et al. [49] have shown that the nature of anions (HCl,  $\text{HClO}_4$ ) not only influences the morphology of PANi tubules but also their oxidation and conformation states. It was proved that in presence of  $\text{ClO}_4^-$  anions, PANi nanotubules exist in a semioxidized polaronic state, and stretched-planar conformation is promoted, while chloride ions favored twisted conformation and quinoid, fully oxidized structure. A very interesting polymer structure was formed during chemical polymerization of P(1,8-DAN) [52] in the acetonitrile solution in the presence of  $\text{FeCl}_3$  as an oxidant. Scanning electron microscopy images revealed that in addition of nanowires, the round shape, so called “desert rose,” structures were obtained, which did not correspond neither to the pore size nor their shape.

One of the advantages of the electrochemical synthesis, when compared with the chemical method, is that the growth rate, length, and thickness of nanotubules and nanofibers can be easily controlled by adjustment of the monomer oxidation potential, deposition charge, and time of polymerization. The electropolymerization of Py and Ani, as well as other monomers, such as Th, MTh, oMA, and 1,8-DAN, was carried out by potentiostatic [57, 66, 67, 80–83], galvanostatic [64, 67–69], or cyclic voltammetry [64, 78, 83] methods. The electropolymerization conditions, such as values of potentials, currents, and composition of polymerization solutions, were similar to those applied in the formation of the three-dimensional bulk polymers. Like in the case of chemical synthesis, the systematic works concerning influence of electropolymerization conditions on morphology of CP nanostructures are scarce. Most of



investigations concerning PPy were carried out by the group of Demoustier-Champagne [62, 63]. In their studies, they investigated the influence of the electrochemical methods (conventional chronoamperometry and pulsed chronoamperometry with different pulse times), monomer and electrolyte concentration, as well as the electrolyte nature. They have demonstrated that PPy nanotubules are formed no matter what conditions are applied. The electro-synthesis method does not change the thickness of the nanostructures. It has also been shown that the increase in monomer and electrolyte concentrations does not affect the thickness of the nanotubules. However, the thickness of the nanotubules increases with the increase in ion size. It is also interesting that the difference in thickness between the different PPy/counterion tubules decreases when the pore size is reduced. The latest works of this group focused on investigation of properties of PEDOT [64] and PANi [57, 80] nanostructures. In contrast to the tubular structures of PPy and PANi, the formation of nanofibers was observed during electropolymerization of ethylenedioxythiophene. The properties of PANi nanotubules [80], such as the molecular and electronic structure, doping levels, and charge carriers, have been investigated by X-ray, Raman, and UV–Vis–near infrared spectroscopies. It has been shown that both the morphology and the intrinsic properties determine the conductivity of the polymer nanostructures.

### Conductivity

It is well-known that the electrical conductivity of any material depends on the carrier concentration and mobility. In the CPs, the carrier (polaron and bipolaron) concentration is determined by the level of oxidation or doping. On the other hand, the carrier mobility depends on the frequency of interchain hopping; therefore, it is related to the conjugation length and the interchain distance. As a consequence, any method of synthesis of CP that enhances molecular and super molecular order leads to an increase in carrier mobility and enhanced electric conductivity. According to Martin [6], enhanced molecular order means the fewer conjugation-interrupting defects in the polymer structure. Whereas, the highly ordered polymer chains results in super molecular order. When a polymer is synthesized within the pores of PC-PTM, the polymer chains are preferentially aligned because of the alignment of the polycarbonate chains in the pore walls. It was also demonstrated that the polymer deposited on the pore walls exhibits an extended conjugation [44]. These improvements in the molecular structure of hard template-synthesized polymers cause the enhancement of conductivity of nanostructures. Another explanation was presented by Granström et al. [60]. They have shown that an increase in conductivity can be regarded as a result of different polymerization conditions in pores of a membrane,

where the concentration of the radicals is lower than the concentration of the monomer. These different conditions within the pores change the polymerization mechanism.

Accordingly, the conductivity of nanostructures can be determined by template (membrane) properties and influenced by the morphology of the formed polymer nanostructures, as well as by the factors, which affect this morphology.

Difficulties in obtaining the absolute values of the electric conductivity were described and discussed by Martin [6, 18] and Duchet et al. [54]. The dependence of conductivity of PPy, PTh, PdMTh, and PEDOT nanofibers [53, 67], as well as PPy and PANi nanotubules [6, 18, 43, 49, 54, 57, 63], on the pore size of PC-PTM was investigated. In general, it was observed that the conductivity of the obtained polymer nanostructures increases with the decreasing pore diameter.

The changes in conductivity were significant. Martin reported that the conductivity of PPy tubules with a diameter about 20–30 nm is over an order of magnitude higher ( $1,000\text{--}2,000\text{ S cm}^{-1}$ ) than the conductivity of electrochemically synthesized PPy films ( $50\text{--}100\text{ S cm}^{-1}$ ). In the case of template-synthesized PANi tubules, conductivity increased from  $9\text{ S cm}^{-1}$  to  $50\text{ S cm}^{-1}$  when tubule diameter decreased from 400 to 100 nm.

Demoustier-Champagne et al. [63] have investigated influence of different counterions applied during electropolymerization of PPy in PC-PTM on morphology and conductivity of nanotubules. They have also observed the conductivity increase with the decrease in tubule diameters. However, for the same tubule diameter, the increase in conductivity was dependent on the size of counterion and was higher in the presence of small ions.

Different results were obtained for the AAO membranes, as it was shown that the conductivity of the PANi nanotubules formed electrochemically in AAO membranes does not depend on the pore size [51]. Conductivity of doped and dedoped PPy, PANi, and PEDOT nanowires and nanotubes obtained electrochemically within the AAO templates was measured before and after dissolution of the template. It was shown that samples within the template exhibit higher values of conductivity than samples extracted from the template [71].

Although the conductivity is a very important parameter, which characterizes the electrical properties of the nanostructures, the comparison of the conductivity values obtained by different methods (i.e., two-probe and four-probe methods) and using different experimental conditions is very difficult and rather of little practical value.

### Concluding remarks

Nanotechnology is one of the most rapidly developing branches of science today, which has also influenced significantly the chemistry of CPs. The increasing number

of published articles, which report studies with respect to preparation and properties of CP nanostructures, demonstrates the extent of this phenomenon. At the same time, it seems that the adventure of the CPs in the field of nanotechnology has only just begun. There are still a lot of studies to be carried out with respect to synthesis and properties of the nanostructured CP, as this material seems to be essential in the further development of functional nanodevices.

The hard template approach to the formation of polymer nanostructures, which was discussed herein, is a fruitful research area. It is a relatively easy synthesis method, which yields a large amount of nanostructures of controlled size and shape. The most important feature of the hard template approach is, however, that it provides the means to control the properties of the obtained nanostructures.

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