Selective Templated Growth of Polypyrrole Strands on Lipid Tubule Edges

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The synthesis of polymers (particularly conducting polymers) in confined areas and volumes is of great interest as a strategy in microstructure and nanostructure fabrication. Our interest is oriented toward the formation of new morphologies created by preferential surface templating. In this report, we describe the polymerization of pyrrole (py) in the presence of diacetylenic phospholipid tubules. These tubules, much studied by Schnur, Yager, and co-workers,[1] are ∼500 nm wide and several micrometers long. Ppy growth is templated specifically on the edges/seams of the tubule and not on its walls. An unusual long strand morphology (10−100 nm wide and micrometers long) results. Attempts to alter the balance between template (i.e., edged-localized) polymerization and solution polymerization reveals that the propensity for template polymerization is overwhelmingly large. The properties of the Ppy thus obtained, and possible templating mechanisms are discussed.

Introduction

Template synthesis has the potential to specifically control the morphology and structure of the resulting polymer or crystalline material. Block copolymers,[2] lipids,[3] and liquid crystals[4,5] have been used as templating media for nanostructured materials. The usual approach is one of conformal templating, where the polymer or crystal growth pattern mirrors the surface of the template. While efforts have been predominantly directed toward conformal templating of inorganic salts, some studies have involved organic crystals[6] and polymers. For example, templating of the conducting polymer polypyrrole (Ppy) has been reported in the presence of microporous polycarbonate membranes,[7] superconductor surfaces ($YBa_2Cu_3O_7$),[8] and single-crystal graphite surfaces.[9,10] An example of a nonconformal templating is the electrochemical synthesis of Ppy on graphite,[10] where templating occurs selectively on the steps and pits of a graphite surface, rather than on the surface itself.

The strand morphology of Ppy is particularly interesting from an applications point-of-view. Strands or filaments have the potential to be used as nanometer-sized wires relevant to electronic devices operating on an extraordinary small length scale.

In this study, we report the template synthesis of Ppy from solution using tubules formed from the diacetylenic phospholipid 1,2-bis(10,12-tricosadiynoyl)-*sn*-glycero-3-phosphocholine ($DC_{8,9}PC$). A striking strand morphology of Ppy is obtained. The strands result from selective templating on the edges of the lipid tubules instead of the tubule surface itself. We show that this nonconformal templating occurs exclusively at these high-energy regions of the surfactant (lipid) surface.

Phospholipid tubules formed from diacetylenic phosphorylcholine have been extensively studied by Schnur, Yager, and co-workers.[1,11−13] These tubules are ∼0.5 μm in diameter and 5−200 μm in length.[12] Tubule formation occurs in two steps: (i) the formation of an intermediate lipid bilayer membrane (bilayer ribbon) and (ii) twisting of the bilayer ribbon into an open helix. The twisted bilayer ribbons close to yield tubules where the bilayer ribbon's edges appear to close and form seams. The driving force for bilayer formation and its twisting into a regular helix is not strongly dependent upon either polar or ionic interactions of the polar headgroups, but is dominated by the diacetylene hydrophobic region.[11] It is not clear whether the edges fuse to form just seams or continue to form a continuous homogeneous surface. Alumina and silica grown on these tubules[14,15] results in a coating over the entire tubule surface, suggesting

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that the tubules are indeed closed, and remain so under reaction conditions. Gold particles grown in the presence of tubules, on the other hand, appear to be selectively deposited along the seams and not the surface.[3]

Experimental Section

Materials. Pyrrole monomer (py) was purchased from Aldrich and used as received. The diacetylenic phospholipid ($DC_{8,9}PC$ >99%) was obtained from Avanti Polar Lipids (Alabaster, AL). Anhydrous ethanol (100%) and is purchased from Commercial Alcohols Inc. Ammonium persulfate was purchased from AnalaR and used as received and $FeCl_3 \cdot 6H_2O$ was purchased from Anachemia Chemicals Ltd and used as received.

Tubules Preparation and Polymerization. Tubules were prepared as per Schnur and co-workers.[1] In a typical preparation, 10 mg of $DC_{8,9}PC$ (1,2-bis(10,12-tricosadiynoyl)-*sn*-glycero-3-phosphocholine) was dissolved in 1.75 mL of absolute ethanol. To this solution was added 0.75 mL of Millipore water (18 MΩ), and the solution became opaque due to the formation of the phospholipid tubules. The wall thickness varies from 10 to 60 nm[16] according to preparation conditions. The mixture was vortexed and centrifuged to precipitate the tubules, and the supernant solvent was then decanted. The precipitated tubules were dried from the ethanol on a filter paper for 10 min after which they were redispersed in 4.5 mL of Millipore water.

Formation of Ppy involved either $(NH_4)_2S_2O_8$ or $FeCl_3$ as initiator. Typically, $(NH_4)_2S_2O_8$ (0.5 mL of 0.05 M, 0.2 M, and 0.8 M) was added to a tubule solution (4.5 mL), after which pyrrole monomer (7.5 μL) was subsequently added. The solution was then gently vortexed for a short time to disperse the pyrrole.[17] Alternatively, pyrrole (7.5 μL) was dispersed in tubule solution (4.5 mL) prior to the addition of $FeCl_3$ (0.5 mL of 0.2 M, 0.4 M, and 0.8 M).

Termination/quenching process resulted from the addition of 8 mL of ethanol to the reaction vessel. Polymerization of pyrrole in ethanol occurs, but only after about 15 h. Other quenching termination routes using sodium bisulfite ($NaHSO_3$), potassium ferrocyanide ($K_4Fe(CN)_6$), and sodium ascorbate did not quench the polymerization but simply slowed it even when excess agent was added. In the case of sodium thiosulfate ($Na_2S_2O_3$), a precipitate is formed and the polymerization is quenched.

Ppy was separated from the $DC_{8,9}PC$ via extraction (5×) using absolute ethanol. In the case of polymerization in the presence of 2 M $NaClO_4$ or $FeCl_3$, 8 mL of Millipore water was added and the solution was then centrifuged. Two additional aqueous extractions were performed, followed by extractions with absolute ethanol (5−7×).

Transmission Electron Microscopy. Transmission electron microscopy was performed using a Philips EM400 at a standard operating potential of 80 kV. The samples were prepared by wicking a droplet of the reaction solution onto a Formvar-coated grid. All images containing only Ppy strands were obtained from ethanol solution, whereas the images containing both lipid and Ppy were obtained from water or water/ethanol solutions. Since the ethanol extracts the lipid and separates it from the polymer, it is not possible to observe the templated polymer with the lipid from an ethanol solution.

FT-Infrared (IR) Spectroscopy. Samples for IR spectroscopy were prepared by pressing 150 mg of KBr with about 1% of Ppy. The IR spectra were obtained using a Bruker IFS 48 spectrometer in transmission mode. The samples were purged with nitrogen for 10−20 min before each measurement. The 1560 cm^{-1}/1480 cm^{-1} dichroic ratio is used as a measure of the conjugation length and there conductivity.

X-ray Diffraction. Samples for X-ray diffraction were dried as a film on a microscope glass and then mounted on a Si (111) holder. The film was attached to the holder by vacuum grease. The grease was scanned in the same conditions of the measurement, and was used as a background substance. The scanning conditions included: θ ranges from 3° to 45° with step widths of 0.02°. The diffraction data were obtained using of Siemens D5000 diffractometer operated at 40 kV/30 mA conditions.

Results and Discussion

The polypyrrole (Ppy) obtained by this templating synthesis is in the form of strands, which have exclusively developed along the tubule seams/edges. (Figure 1). Different polymerization times yield different strand thicknesses, ranging from ∼10 nm (2 min) to 60 nm (15 min). When $S_2O_8^{-2}$ is the initiator, the polymerization process is complete after ∼15 min.

The method used for tubule preparation leads to different types of tubules. Templated Ppy reflects this diversity (Figure 1A), and the way in which Ppy decorates the tubules can help us understand both the templating phenomenon and the tubules themselves. As the lipid ribbon becomes a tubule, the ribbon edges approach one another. This open tubule (Figure 1B) thus has two parallel bilayer edges exposed to the solution. Ppy grows on each of these edges, and the two Ppy strands track one another. The end of a tubule is also a well-defined edge, and Ppy rings (∼400−500 nm diameter) frequently form there. Even tubules that have no other Ppy on their edges or seams (Figure 1C) will often have an end ring. The tubule end, unlike a seam, has a permanently exposed bilayer edge. Seams however could be so tightly fused that a homogeneous surface is created. A fully formed tubule with active seams creates a single Ppy strand that decorates the tubule in a helical manner (Figure 1D). Because tubule walls are made of many concentric bilayers and not just a single one, each bilayer can be decorated separately (Figure 1E). It is important to note here that in all cases the resulting Ppy is a continuous material (Figure 1F).

Evaluation of the conjugation length of the Ppy strands was performed by IR as per Martin et al.,[18] based on a study by Zerbi et al.[19,20] The ratio of the infrared peak intensities at 1560 cm^{-1} and 1480 cm^{-1} for the Ppy sample is used as a measure of the conjugation length and thus the conductivity, as it is proportional to the extent of delocalization resulting from oxidative doping.[18] IR spectra of the Ppy ($S_2O_8^{-2}$ initiation, polymerization time of 15 min) formed with and without lipid yield quite similar IR dichroic ratios. The actual Ppy structure in the 10−100 nm wide strand is most likely similar to "bulk" Ppy. The template-grown Ppy, prepared using different polymerization times is amorphous (as determined by powder X-ray diffraction) with no notable differences from the bulk Ppy. TEM images show that the strands have jagged edges, which is not expected for a fiber structure.[21]

It is important to understand how and why the polymerization process is exclusively templated on the nascent edges (or seams) rather than the continuous surface of the lipid tubule. The lipid surface clearly

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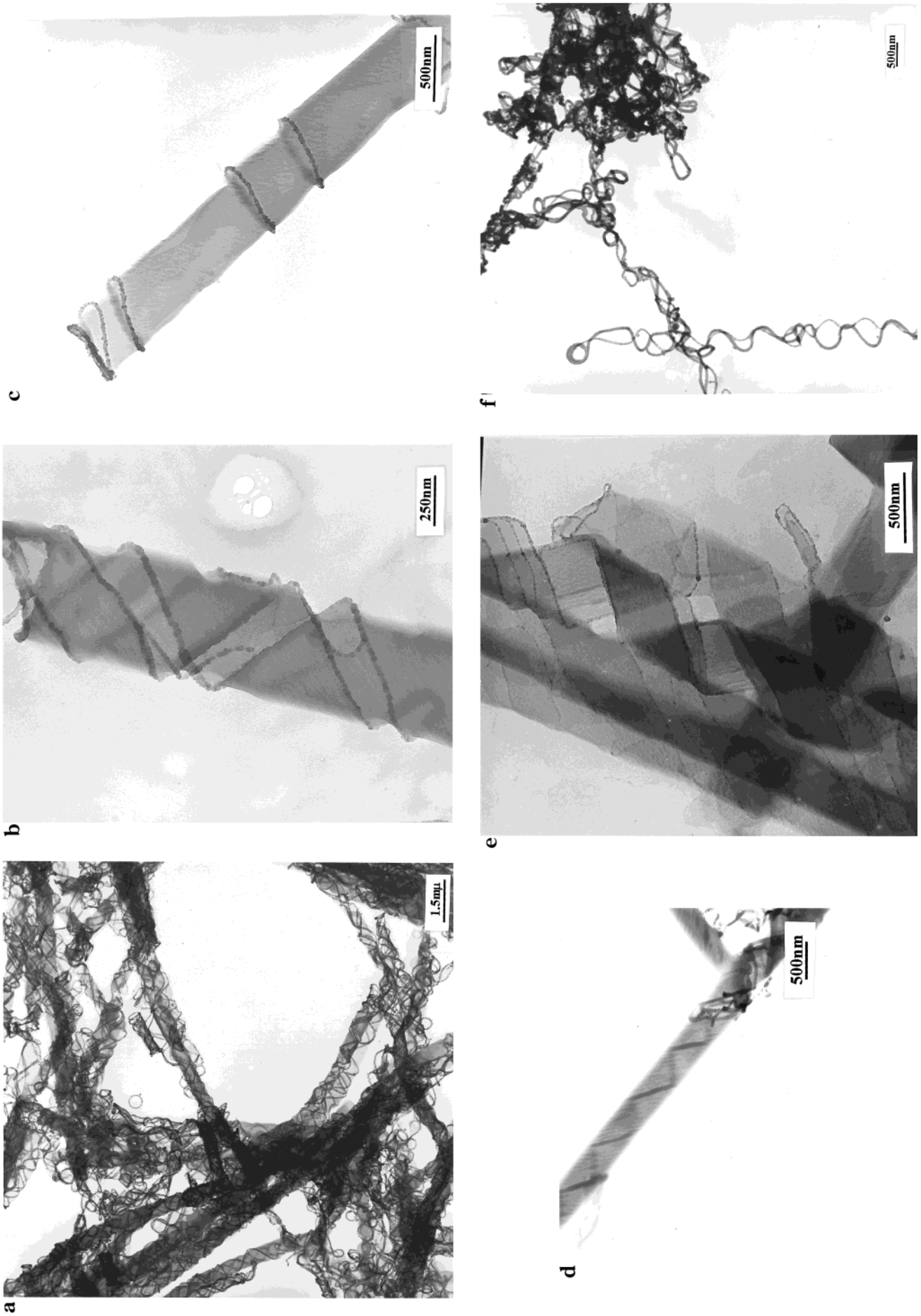
a
1.5μm
b
250nm
c
500nm
d
500nm
e
500nm
f
500nm

Figure 1. Ppy strands formed on $DC_{8,9}PC$ tubules. In A−E, the Ppy appears on the lipid tubules. The faint gray regions are the lipid tubules themselves and the dark-gray/black lines are the Ppy strands. Part A: Overall appearance of Ppy templated on the $DC_{8,9}PC$ tubules. Note the variety of phenomena appearing in the image. One observes individual Ppy rings, rings at the end of the tubules, open tubules with strands tracking one another, and open tubules with several lipid bilayers evident. The image also reflects the way the templated tubules are cast on the TEM grid. Polymerization conditions: 0.02 M $(NH_4)_2S_2O_8$, 0.02 M py, 2 mM $DC_{8,9}PC$, 15 min. Part B: Ppy templated on an open tubule. Polymerization conditions: 5 mM $(NH_4)_2S_2O_8$, 0.02 M py, 2 mM $DC_{8,9}PC$, 15 min. Part C: Four concentric tubule bilayers, each inside the next, decorated at the end with Ppy rings. Note the difference in the diameter and the intensity (contrast) of the gray color of the lipid tubule. The outermost tubule (with the largest ring diameter) has the most contrast. This is because the more bilayers there are the greater will be the contrast in the TEM image. Polymerization conditions: 0.02 M $(NH_4)_2S_2O_8$, 0.02 M py, 2 mM $DC_{8,9}PC$, 4 min. Part D: A single strand of Ppy on a closed tubule. Note that only one strand appears. Polymerization conditions: 5 mL of tubules in ethanol/water solution incubated with 2 mL of 1 M$(NH_4)_2S_2O_8$ for 20 min, then centrifuged to remove supernant. A total of 10 mL of water was added, followed by addition of 15 μL of py. Polymerization time: 30 min. Part E: Open helical ribbon where on top of the image there are four bilayer membranes, each of them decorated with Ppy on their edge. Note that the Ppy decorates each bilayer edge separately, and that the four bilayers become two (middle of image). Polymerization conditions: 0.02 M $(NH_4)_2S_2O_8$, 0.02 M py, 2 mM $DC_{8,9}PC$, 4 min. Part F: Isolated Ppy strands extracted from the tubules. Polymerization conditions: 0.02 M $(NH_4)_2S_2O_8$, 0.02 M py, 2 mM $DC_{8,9}PC$, 15 min.

offers two locations where the reaction could occur: the lipid tubule surface and its edges. The edges might have more exposed acyl chains than does the surface. The electron-rich acetylene groups may play a significant role in the adsorption of the pyrrole onto the edges. The edges may thus offer chemically preferred sites for adsorption between py, $py^{+\bullet}$, and initiator and the acetylene groups. Donor−acceptor processes are the likely source of interaction. Although the detailed structure of the edges is not known, they clearly are high surface energy sites and are probably hemispherical. An edge is also a physically preferred site due to the high surface energy associated with the curved edges. These two properties evidently make the seams/edges much better candidates for adsorption than the tubule surface.

Ppy prepared in the absence of the tubules is in the form of aggregates of spheres, with sphere diameters of 80−200 nm. It is noteworthy that a Ppy film coats the reaction vessel walls (glass or polypropylene) in the absence of the $DC_{8,9}PC$, whereas negligible coating occurs in the presence of the lipid tubules.

The Ppy strands appear to be made up of coalesced beads, suggesting that a nucleation and growth mechanism occurs. To probe the growth mechanism of this Ppy, polymerization reactions were performed in aqueous solution at high ionic strength, with two different initiators and several initiator concentrations. High ionic strength tests whether electrostatic screening of the growing cationic polymer reduces nuclei−nuclei distances. The strands obtained by polymerization in 2 M $NaClO_4$, are smoother than that of the jagged-edged strands synthesized in the absence of electrolyte. This material is amorphous and the strand thickness remains ~60 nm. Early coalescence made possible by the screening of charges on the nuclei evidently leads to these smoother Ppy strands.

Polymerization with a reduced quantity of initiator (5 mM of $S_2O_8^{-2}$ or 20 mM of $FeCl_3$) and 0.02 M pyrrole results in formation of thinner strands (20−30 nm). Boundaries or gaps between the spheres aligned along the tubule edges appear under these conditions. Polymerization using a large initiator/py ratio results in strands with a distribution of thicknesses. The same initiator/py ratios were also used with a 4-fold increase of the $DC_{8,9}PC$ lipid. The resulting Ppy is similar in appearance, but in general is thinner. If a small initiator concentration is used in conjunction with large lipid concentration, then complete gaps appear between the spheres (Figure 2).

The combination of a large initiator quantity and high ionic strength yields "smooth" strands. These are rather inhomogeneous in thickness and have separate spheres attached to them (Figure 3). This is true at both high and low lipid concentrations. The attached spheres appear less frequently if using a high (i.e., 4-fold increased) lipid concentration.

$FeCl_3$-initiated polymerization is slower[22] than the $(NH_4)_2S_2O_8$ initiated process and the $FeCl_3$ -generated material has a rougher morphology. The strands resemble a bead necklace with similar or slightly lesser final diameters than observed for the short time (15

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Figure 2. Separated beads of Ppy on a tubule. Note the separated beads on the tubule edges, with diameters ranging from 10 to 20 nm. The lipid ribbon (helix) that covers the closed tubule on the left-hand side of the image has been decorated along both its edges by Ppy. Polymerization conditions: 5 mM $(NH_4)_2S_2O_8$, 0.02 M py and 8 mM $DC_{8,9}PC$ in Millipore water, 15 min.

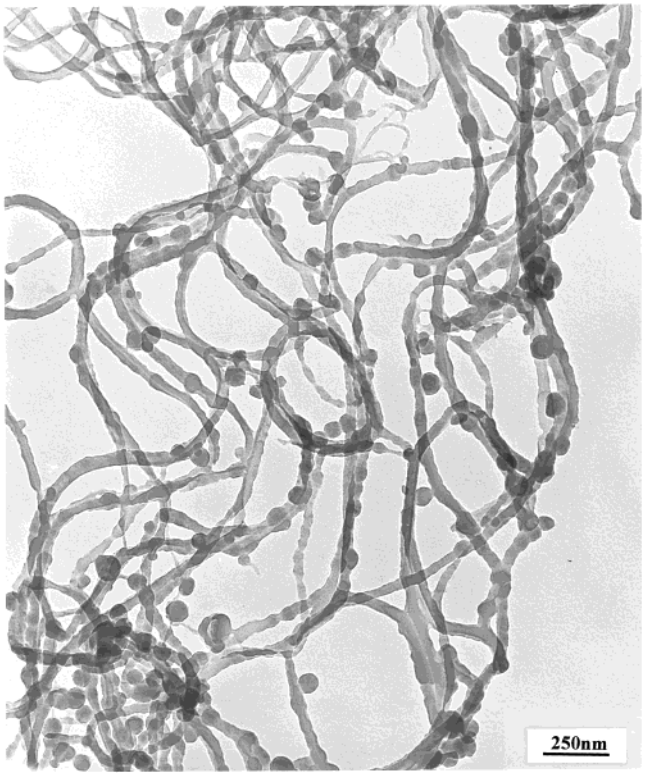

Figure 3. Separated spheres with close proximity to Ppy strands. Isolated Ppy strand extracted from the tubules. Note the variety of thicknesses. Polymerization conditions: 0.08 M $(NH_4)_2S_2O_8$, 0.02 M py, and 8 mM $DC_{8,9}PC$ in 2 M $NaClO_4$ solution, 15 min. Ppy strands were extracted from the lipid using ethanol.

min) $(NH_4)_2S_2O_8$-generated material (Figure 4). The strands prepared using $FeCl_3$ and long reaction times are thicker than those obtained using $S_2O_8^{-2}$ as initiator.

Scheme 1 describes the complex interplay between physical (partitioning) and chemical (polymer growth) processes in this system. Control of the resulting polymer can in principle be achieved by "tuning" the relative rates of these processes. It is worth emphasizing that despite many attempts to change the balance between templated polymerization to solution polymerization, the propensity for template polymerization is overwhelmingly large. The kinetic advantage is clearly so large so as to make the system very robust toward strand formation.

Ppy formation is an addition polymerization process, proceeding from the oxidation of the pyrrole monomer by an initiator ($FeCl_3$ or $(NH_4)_2S_2O_8$), and creation of a radical cation.[23,24] This radical cation initiates the polymerization and can be regarded as a nucleation center. This nucleation center can then react with another radical cation via radical−radical coupling[23] (with rate constant $k_{py^{+\bullet}}$) or with another monomer by radical−monomer coupling[24,25,26] (with rate constant k_{py}). The number of nucleation centers on the lipid edges will be proportional to the quantity of initiator, which in turn is proportional to the instantaneous $[py^{+\bullet}]$ in the system.

The polymerization can begin either in the solution or an edge. If the equilibrium constant for the adsorption of the py to the tubule edge is greater than that of the radical−cation $py^{+\bullet}$, or if the initiator adsorbs to the edges the polymerization will begin on the edge. Edge-initiated polymerization could arise if the initiator partitions strongly into the lipid edge, and the polymerization is thus localized there. However, both initiators used here are salts, and are expected to predominantly reside in the water phase.

Alternatively, edge-initiated polymerization arises because neutral py has limited solubility in water and will thus seek a hydrophobic-like adsorption site. If the tubule edges are more hydrophobic than the tubule surface, the py monomer will be concentrated on the tubule edges, and polymerization will progress there. Faster growth of Ppy on a hydrophobic surface has been noted previously by Whitesides and co-workers.[2] The balance between solution polymerization and edge-localized polymerization can be studied using a high concentration of initiator. This will create a situation where the surface becomes saturated with $py^{+\bullet}$ and excess $py^{+\bullet}$ escapes from the surface, allowing some

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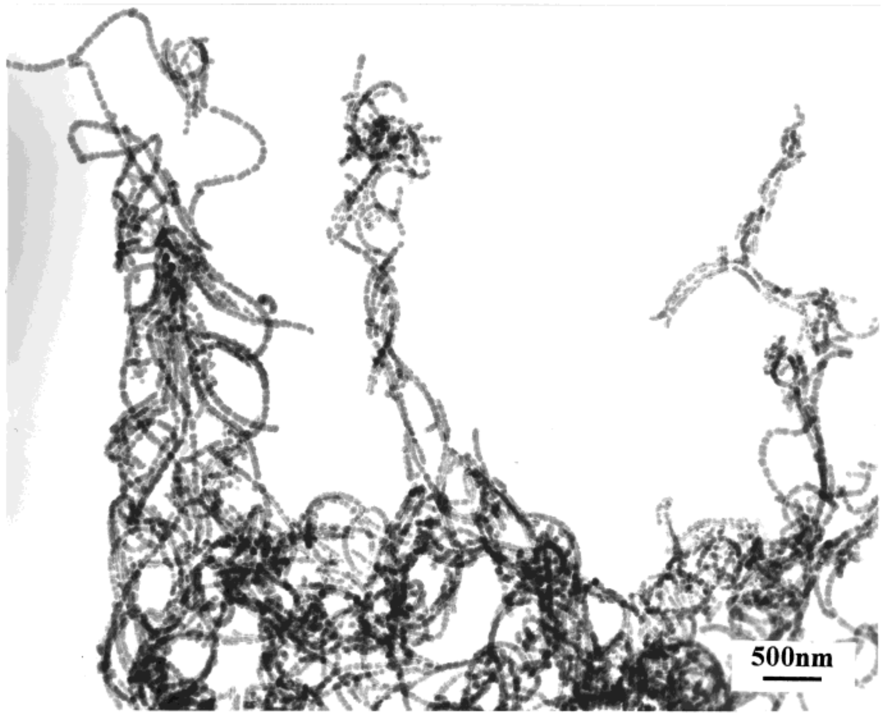
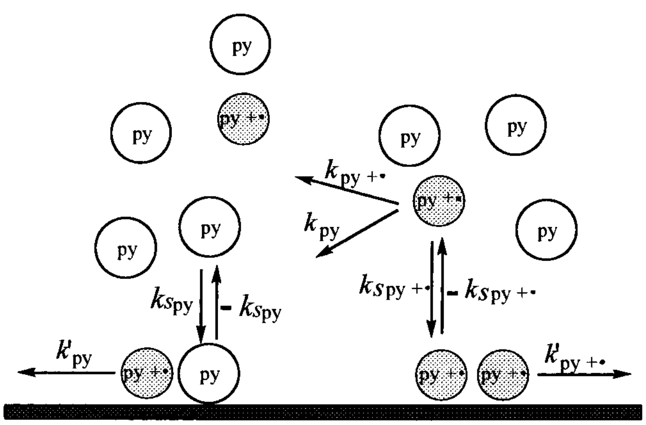


Figure 4. Strands formed using $FeCl_3$ as initiator. Isolated Ppy strand (prepared using $FeCl_3$ as initiator), extracted from the tubules. Note that the strand obtained looks like a necklace of Ppy beads, but is still a continuous material. Polymerization conditions: 0.08 M $FeCl_3$, 0.02 M py, and 2 mM $DC_{8,9}PC$ in water solution, 20 min. Ppy strands were extracted from the lipid using ethanol.

Scheme 1. Description of the Competing Processes in the Template-Directed Polymerization Process[a]



[a] Abbreviations: py, pyrrole; $py^{+\bullet}$, pyrrole radical cation (oxidized pyrrole); k_{py}, rate constant of the radical−monomer coupling in solution ($py^{+\bullet}$/py coupling); k'_{py}, rate constant of the radical−monomer coupling on the surface; $k_{py^{+\bullet}}$, rate constant of the radical−radical coupling in solution ($py^{+\bullet}/py^{+\bullet}$ coupling); $k'_{py^{+\bullet}}$, rate constant of the radical−radical coupling on the surface; k_{spy}, rate constant of adsorption of py monomer onto the surface; $k_{spy^{+\bullet}}$, rate constant of adsorption of $py^{+\bullet}$ onto the surface; $-k_{spy}$, rate constant of desorption of py monomer out of the surface; $-k_{spy^{+\bullet}}$, rate constant of desorption of $py^{+\bullet}$ out of the surface. Template surface in this regard is a tubule edge. There may be adsorption onto the tubule surface as well, but because polypyrrole is observed only on the tubule edges, we will regard it as the only template surface of importance in this description.

polymerization in solution to occur as well (Figure 3 see further discussion). However, the close analogy between emulsion polymerization and our system[27] leads us to favor the solution as a starting point for nucleation. In our case developing Ppy spheres (nucleation centers) precipitate out from solution, and selectively deposit onto the lipid edges.

The solution-initiated polymerization process involves competition between solution polymerization and adsorption of the radical cation $py^{+\bullet}$ onto the tubules edged surface. Given that Ppy strands appear on the tubule edges even at very short reaction times (i.e., 2 min), the adsorption rate is apparently fast compared to solution polymerization. A 2 min polymerization time yields a 10 nm thick Ppy strand. This corresponds to a strand thickness of about 20 py units.

Polymerization under conditions of high ionic strength and large initiator quantity enhances the extent of the $py^{+\bullet}/py^{+\bullet}$ coupling. High ionic strength screens the charge on the $py^{+\bullet}$, leading to an increase in $k_{py^{+\bullet}}$, and facilitates the coalescence of adjacent Ppy nuclei ($((py)_n{}^{+\bullet})$) which reside on the lipid edge. High ionic strength/large initiator concentrations thus enhance the solution-based $py^{+\bullet}/py^{+\bullet}$ coupling process because of a concurrent increase in both the rate constant and concentration. (Separate polymer spheres are obtained in close proximity to the strands.) Under these conditions spheres correspond to polymerization in solution, whereas "smooth" polymer strands correspond to polymerization on the lipid edges (Figure 3).

The competition between polymerization initiation, propagation, and termination rates is the primary determinant of the size of the Ppy spheres. Small initiator concentrations (5 mM) results suggest that an active termination process occurs. This termination process (possibly a nucleophilic attack of water on Ppy cation[18]) proceeds at a constant rate. As the initiation rate decreases, the propagation to termination rate ratio

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also decreases, yielding shorter chains, or in this case smaller spheres. Coalescence of these smaller spheres leads to thinner Ppy strands.

Conclusion

We observe a highly selective, nonconformal growth of Ppy on the *edges*, rather than on the *surface* of the phospholipid tubules. IR spectroscopy and powder X-ray diffraction studies show that the polymer formed in the presence of the lipid is similar to that prepared in bulk solution. Details of the morphology of the polymer obtained are governed by the polymerization conditions. In particular, the nature of the initiator and the initiator/monomer ratio are crucial in determining the eventual polymer morphology.

Once nucleation centers are deposited on the tubule edges, the propagation process occurs by diffusion of py or py radical cation into these growing nucleation centers either from solution, or from the tubule surface, and continues to grow there. The species deposited on the edges is not an individual molecule but instead is a growing nucleus because of competition issues. It thus may not be possible to grow strands with core structures comprising parallel chains of Ppy on the tubule edges. To do so, an *individual* py or $py^{+\bullet}$ species has to react with another edge-localized molecule, before it will react with another individual py molecule in solution.

Ongoing work in our laboratory is oriented toward understanding the interesting chemistry of the tubule edges.

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