

SYNTHESIS AND CHARACTERIZATION OF POLYPYRROLE NANOWIRES USING ALTERNATING AMPHIPHILIC COPOLYMER NANOTUBES AS TEMPLATES

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ABSTRACT

It has been reported that poly(styrene-*alt*-maleic anhydride) (SMA) chains would self-assembled into a nanotube in aqueous solution at pH7 by associating through a linear conformation which favours the association of the chains by decreasing the entropic cost due to H-bonding and π -cation interactions. The combined theoretical and experimental characterization of the nanotube revealed that the interior of the tube is hydrophobic while the exterior is hydrophilic. With this property in mind, we developed a method for fabricating intrinsically conducting nanowires. The nanowires are synthesized inside the hydrophobic cavity of the polymeric nanotubes. However, the solubilization of small organic molecules containing benzene groups disrupts the π - π interactions within the tubes and therefore breaks the tubular structure. In order to generalize our method to small organic molecules containing benzene group, we choose a new alternating copolymer poly(isobutylene-*alt*-maleic anhydride) (IMA). We will present the characterization of the solubilization and polymerization of pyrrole with the nanotube template by a combination of experimental (DLS, SANS, UV-Vis, and IR) and theoretical methods. The careful and precise characterization of the synthesis of well-defined, high density conducting nanowires can have a major impact for applications in nanoelectronics and development of sensors.

Keywords: copolymer, template, nanowire, IMA, pyrrole.

1 INTRODUCTION

New nanomaterials already play a key role in several emerging technologies such as nanomotors, nanoelectronics [1] and drug delivery [2]. To develop new nanomaterials tailored to specific application, we propose to base our approach on a model that we have carefully investigated and applied to nanowire synthesis [3]. Indeed, we have characterized a novel self-assembly process for biocompatible alternating copolymers into nanotubes. The self-assembly process was illustrated by the association of 8 poly(styrene-*alt*-maleic anhydride) (SMA) chains into a nanotube [4] in aqueous solution at pH7. The combined characterization of the nanotube revealed that the interior of

the tube is hydrophobic while the exterior is hydrophilic (Figure 1). With this property in mind, we developed a method for fabricating intrinsically conducting nanowires [3]. The nanowires are synthesized inside the hydrophobic cavity of the polymeric nanotubes. This method is environmentally-friendly and efficient to synthesize well-defined, high density conducting nanowires which cannot be synthesized in the absence of polymeric nanotubes as a template.

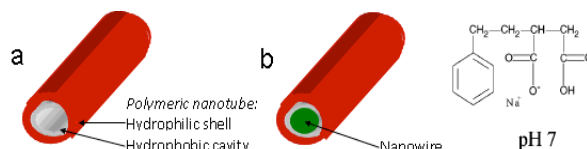


Figure 1: Pictorial representation of a) SMA nanotube, and b) hydrophobic nanowire within the SMA nanotube.

However, the solubilization of small organic molecules containing benzene groups disrupts the π - π interactions within the tubes and therefore breaks the tubular structure. In order to generalize our method to small organic molecules containing benzene group, we choose a new alternating copolymer: poly(isobutylene-*alt*-maleic anhydride) (IMA). IMA is also a water-soluble polymer and has the same properties as SMA (Figure 2): indeed, its structure is pH-dependent due to the maleic anhydride ring [5]. The main difference between the two compounds lies in the hydrophobic group of the copolymer; SMA contains a benzene ring. The theoretical and experimental (DLS) study of this copolymer shows the same stiffening of the polymer backbone at pH7 [6] which favours the association of the chains in water to minimize the contact between the non-polar groups of the polymer with the solvent (water) by decreasing the entropy cost the association.

We will present the characterization of the solubilization and polymerization of pyrrole with the nanotube template by a combination of experimental and theoretical methods. The polymerization of the polypyrrole nanowire was followed by UV-Vis spectroscopy. A change in structure after complete polymerization was also observed using Dynamic light scattering (DLS) and Small Angle Neutron Scattering (SANS). We will also present the vibrational frequencies of polypyrrole obtained using

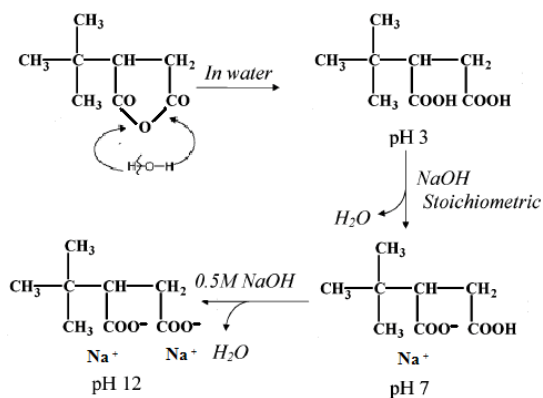


Figure 2: Structure of isobutylene-maleic anhydride at different pH values.

theoretical computations and compared to IR spectra taken from our samples. The careful and precise characterization of the synthesis of well-defined, high density conducting nanowires can have a major impact for applications in nanoelectronics and development of sensors.

2 METHODS

2.1 Sample preparation

The polymers were purchased from Aldrich Co. and have molecular weights of 6,000 and 350,000 for IMA (~85% purity) and SMA (~85-90% purity) respectively. Low concentrated (0.05% wt in deionized water) amphiphilic copolymer nanotube solutions of IMA and SMA were prepared and then sonicated for a few hours (2-3 hours for SMA and 6 hours to 1 day for IMA). The pH of the solution was adjusted to 7 by stoichiometric addition of sodium hydroxide.

For each 10 ml sample of polymer solution, 0.5 ml of pyrrole was added. In addition, a control experiment was performed; 0.5 ml of pyrrole was added to 10 ml of water. The three samples were gently sonicated for one minute and left to stand. The solutions were centrifuged at 14,500 rpm for 30 minutes prior to analysis.

2.2 Nanotube and Nanowire Characterization

The radius of gyration of the copolymer nanotubes templates and the filled nanotubes was measured in water using DLS (Brookhaven model 9025) equipped with 632.8nm He-Ne laser. The measurements were taken at a 90° angle. The samples were filtered using filters with a pore size of 0.4-0.5µm.

SANS experiments were carried out on the NG3 30-m Small Angle Neutron Scattering Instrument at the NIST research reactor in Gaithersburg, Maryland. The incident wavelength was 6Å, and the sample aperture was 10*10mm². The resulting Q range was 0.03 to 0.40 Å⁻¹. The

experiment was carried out using deuterated water as the solvent to increase the contrast. Deuterated pyrrole was added to the polymer sample in order to analyse the copolymer nanotube at various stages of the pyrrole polymerization.

UV-Vis and IR spectra of the polymer samples in solution were also taken.

3 RESULTS AND DISCUSSION

Pyrrole is a yellow hydrophobic organic liquid. Hence, when added to water, the organic compound forms a layer over the solvent. With the presence to the copolymer nanotubes, we predicted that pyrrole would solubilize by entering the hydrophobic cavity. From there, the organic compound would polymerize to form the nanowire.

Half an hour after the addition of pyrrole to the IMA and SMA solutions, both copolymer samples were cloudy and showing signs of precipitate. Also, the organic-aqueous bi-layer had disappeared. On the other hand, no changes were observed with the control sample of water. As time progressed, the IMA sample became less cloudy and blue with a formation of yellow/brown precipitate on the walls (Figure 3). The SMA sample was still cloudy and yellow. This indicates that both polymer solutions are capable in altering the organic compound, but the kinetic processes are different.

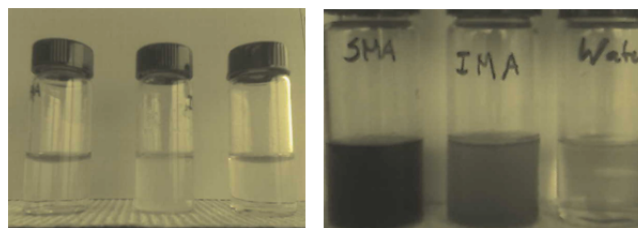


Figure 3: (Left) Samples of SMA (left), IMA (middle) and water (right) after the addition of pyrrole; (Right) SMA and IMA solutions and water, three days after the addition of 0.5ml of pyrrole.

UV-Vis spectra were taken of all three samples at various time frames: before the addition; one day after the addition; and one week after the addition. From the reduced plot, a significant red-shift along the peaks with increasing time is observed for all samples including water. However, only the copolymer solutions show a growing shoulder at lower energy from the original peak. This shoulder growth is indicative of pyrrole polymerization [7]. Further analysis was performed on the IMA with pyrrole sample (Figure 4).

SANS, a key technique for the study in complex fluids and polymers, provided detailed information on the structure of the IMA nanotube template during the same polymerization stages of the UV-Vis experiment (Figure 4). At low Q range (0.004-0.01Å⁻¹), there is a significant decrease in the slope; at mid Q range (0.01-0.1Å⁻¹), a shoulder forms after complete polymerization (one week).

The appearance of the shoulder at the same mid Q range is similar to that observed in an analysis of SMA [8]. SMA was determined, using a model fitting [9-10], to have a tubular structure with inner radius of $13.0 \pm 0.8 \text{ \AA}$ and outer radius of $19.9 \pm 1.5 \text{ \AA}$ for concentration 0.05% wt. This suggests that the structure of the fully polymerized pyrrole with IMA is tubular as well. The IMA samples were quite diluted; hence, the scattering intensities were not as intense.

Several different models were fitted to this data set, and so far the only model that yields the most statistically acceptable result is the flexible cylinder of polydispersed radius [11-12]. Using this model, we indeed do observed a decrease in radius of gyration due to the change in slope. More model fitting is currently being performed to characterize this system.

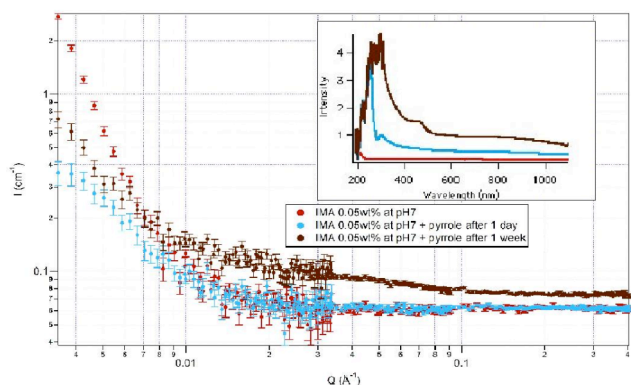


Figure 4: (Bottom) SANS data of 0.05 wt% IMA with addition of pyrrole at varying stage of polymerization; (Top) UV-Vis spectra of the same samples. The increasing shoulder at 480nm confirms the polymerization of pyrrole.

The hydrodynamic radius was also obtained on all nanotube samples using DLS. The results are displayed on Table 1. The addition of pyrrole to the nanoparticle solution has decreased the size of the association. This may be a sign that the polymerization occurs on the inside of the tube instead of the outside; however, this cannot be confirmed until more study has been made.

Sample	Eff. Diameter (nm)	Poly. Dispersity
IMA 0.05%wt pH 5	258.9	0.1429
SMA 0.05%wt pH 5	20.8	0.1561
IMA 0.05%wt Added pyrrole	67.0	0.2140
SMA 0.05%wt Added pyrrole	18.2	0.2406

Table 1: The effective diameters and their respective polydispersity of all copolymer solution samples. The products of the pyrrole had to be diluted for practical reason; the real concentration is estimated to be $\sim 0.02\%$ wt.

IR spectroscopy is a tool widely used to study the interaction between molecules. It is a significant tool in this case since it will be able to reveal the nature of the polymerization: whether the polymerization occurs on the outside or the inside of the amphiphilic copolymer nanotube. Non-water soluble ZnS crystall windows (~ 700 - 4000 wavenumber) were used to hold the sample since drying the samples would disrupt the structure of the amphiphilic copolymer leading to misleading information on the interaction with polypyrrole.

When comparing the spectrum of the IMA copolymer solution to those polypyrrole and the nanostructure (Figure 5), a sharpening of a band at 3400 cm^{-1} is observed and has moved to 3300 cm^{-1} . This represents the N-H bond of the pyrrole. Sharp peaks appear at 750 , 1034 , 1067 , and 1085 cm^{-1} for the polymer solution with added pyrrole. Overlapping bands also appear at the 2000 - 3000 wavenumber region. These bands are particularly difficult to analyze and are most likely the interaction frequencies of interest. The sharp peak at 1680 cm^{-1} remains unchanged; this represents the stretching to the carboxyl group of the copolymer.

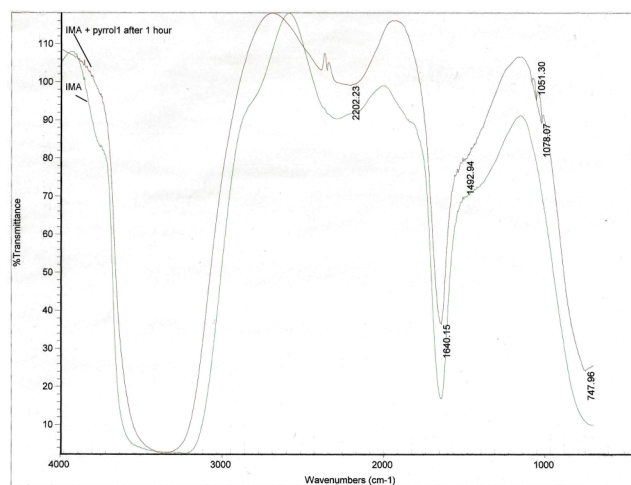


Figure 5: Raw IR spectrum of 0.05 wt% IMA solution (green) and 0.05% wt% IMA solution after 1 hour of the addition of pyrrole (red). Sharp peaks appear at 750 , 1034 , 1067 , and 1085 cm^{-1} . A shift in the band appears in the 2000 - 3000 wavenumber region. Overlapping bands become noticeable after further polymerization.

In order to analyze this spectrum, we use the results obtained from the computation method as a comparison. Since the full optimization of IMA has yet to be completed, we used the results of pyrrole and polypyrrole (optimization and frequency calculation at the PM3 level of theory [13-14]). The IR spectrum of pyrrole obtained using theoretical methods is comparable to the experimental spectrum (Figure 6). The values of the theoretical spectrum match those of the practical within a few wavenumbers (~ 5 - 20). This difference in wavenumber and in the broadening of the peaks for the experimental data are most likely due to the

environmental condition [15] at which the spectrum was taken; however, the overall agreement between simulation and experiment data is very good. Hence, the IR spectrum obtained from theoretical methods is an excellent means of comparison to the copolymer-pyrrole spectrum.

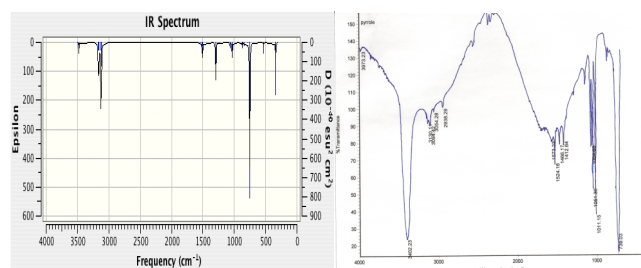


Figure 6: (Left) IR spectrum of pyrrole obtained from the optimization of pyrrole at the PM3 level of theory; (Right) Raw IR spectrum of pure pyrrole. Sharp peaks appear at 750, 1034, 1067, 1085 and 1500 cm^{-1} . The values of the peaks for both spectra closely match.

The sharp peaks appear at 750, 1034, 1067, and 1085 cm^{-1} represent stretching from the polypyrrole itself. However, on both the computational and experimental spectra of pyrrole and polypyrrole, there is a strong sharp peak at 1500 cm^{-1} originating from a nitrogen stretching (Figure 7). This peak is absent on the copolymer-polypyrrole spectrum. This suggests that this particular stretching is obstructed during the polymerization phase.

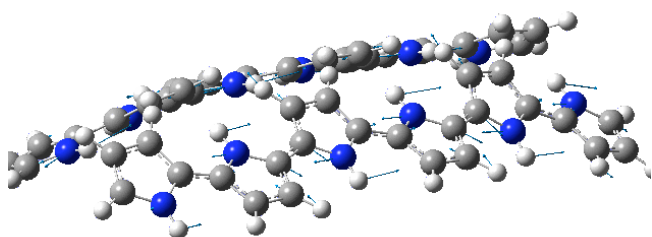


Figure 7: Representation of the absent stretching (1500 cm^{-1}) in the IMA with addition of pyrrole IR spectrum.

4 CONCLUSION

It was suggested that the IMA nanotubes can be used as a template to synthesize polypyrrole nanowires. This is well-known for the SMA nanotubes. It was observed, however, that the polymerizing rate for both copolymer templates is different. UV-Vis spectrometry monitored the aggregation of the organic compound, whereas SANS monitor the structure of the nanotube template. The data obtained from the SANS analysis is consistent with the results of the DLS: the size of the nanotubes did decrease with the polymerization of pyrrole. The mechanics of the growth was analyzed using IR spectrometry. The results

indicate that the nanotubes might be hindering one particular stretch of the polypyrrole within the tube.

Understanding the mechanism that allows such hydrophobic organic compounds to solubilize in water and form nanowires would have great implications in the field of nanotechnology. In addition, since these copolymer nanostructures are able to solubilize small organic structure, it may also be possible to solubilize larger structures such as single wall carbon nanotubes. This has particular interests for such applications like storage.

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