

Synthesis of Polypyrrole within Polymeric Nanotemplates in Aqueous Environment

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ABSTRACT

Amphiphilic alternating copolymer poly(styrene-alt-maleic anhydride) (SMA) was reported to be used as nanotemplates to fabricate polypyrrole nanowires in aqueous environment. Previously we studied the mechanism of polypyrrole synthesis through *ab initio* computational calculations [1]. We concluded that both water and confinement effect of the nano templates have impacts on polypyrrole synthesis. In this paper, we will use experimental characterization techniques such as IR, UV-vis, TEM, DLS and SANS to confirm the theoretical calculation and explore the confined environment impact on polypyrrole synthesis.

Keywords: polypyrrole, confinement effects, nanotemplates, polystyrene-block-polyacrylic acid (PS-b-PAA)

1 INTRODUCTION

Conductive polymers, such as polyaniline or polypyrrole are attractive building blocks for several applications [2-3]. Polypyrrole is one of the most studied conducting polymers due to its good electrical conductivity, environmental stability and relatively easy synthesis [4-7]. Earlier we reported an innovative way of synthesizing polypyrrole within nanotemplates in aqueous solution with controlled morphology [8,9]. When immersed in the template, pyrrole molecules polymerize in the hydrophobic cavity, with no external inductions. The soft templates provide a confined environment for the synthesis where the reaction did not occur in bulk solution. In previous study, a thorough *ab initio* quantum chemical study of the polymerisation mechanism calculated the structures and the energies of the essential intermediates and products. This study proved that water was crucial in activation and the polymerization process [1]. However, the role of confinement effect remains unanswered. The influence of the confined templates has attracted increased interests because the systems where these materials are being considered as nanoscale templates for various nanotechnology fabrication applications. The confinement effect, has been widely reported in systems such as carbon nanotubes [11], amphiphilic copolymers [10] and zeolite [12] and studies show that confined environment results in dramatic change in dynamic and thermodynamic properties of fluids [13]. In our case, the reaction would not occur in bulk water

solution without the confined templates (2nm in diameter) implies having a limited space is crucial for the reaction to occur. Therefore we are interested in establishing the influence of the confinement effect on the polymerization. The aim of this study is to confirm the theoretical results using experimental characterizations such as UV-vis, IR spectroscopy and TEM. The present paper will also present the role of confinement effect by studying the reaction in similar system of different dimensions.

2 EXPERIMENTAL

2.1 SMA nanotube preparation

Poly(styrene-alt-maleic anhydride) SMA was purchased from Aldrich Co. and have molecular weight of 6,000g/mol. The samples were dissolved in water at 1 wt.% and it was neutralized by adding equimolar amount of NaOH. The solution was then sonicated over night.

2.2 Preparation of block copolymer templates

PS-b-PAA (Polystyrene-b-poly(acrylic acid)) was purchased from polymer source (Mn=16000-b-3500). The block copolymer was first dissolved in THF, which is a common solvent for both blocks in 0.1wt. % or 0.5 wt. %. Subsequently, deionized water was added to the polymer-THF solution dropwise at a very slow rate with vigorous stirring. As the addition of water progressed, the quality of solvent for polystyrene decreased gradually. The addition of water was continued the water content reached certain concentration (90 wt.%,97 wt.%), place the solution in dialysis bags and dialyzed against water over night to remove the solvents. In the present study, three samples sample 21 (0.1 wt.% THF, 97 wt. % water), 22(0.1 wt.% THF, 90 wt. % water) and 23 (0.5 wt.% THF, 90 wt. % water) were prepared to achieve different cavity dimensions.

2.3 Pyrrole polymerization

The pyrrole monomers were purchased from Aldrich and it was used directly without further purification. Pyrrole was added dropwisely into the SMA or PS-b-PAA solution at 1.2 equivalent volume of the template cavity. Pyrrole was allowed to diffuse at room temperature for a week without any other external disturbance.

2.4 UV-vis

The formation of polypyrrole was investigated by recording UV-vis spectra on a UV-240 spectrometer. UV-vis spectra were taken during the polymerization in the nanotemplate at various time frames.

2.5 Infrared Spectroscopy

Infrared spectroscopic measurements were performed on SMA template systems using Bruker Spectrometer model VECTOR22. The solution was treated with strong acid (HCl) or base (NaOH) to remove the polymeric templates. Once the pH was changed, a precipitate formed at the bottom. The solid precipitate was extracted from the solution and dried in the oven over night. The dried powder was mixed with KBr, pressed as KBr pellets.

2.6 Transmission Electron Microscopy

The morphology of prepared PPy samples was studied by TEM. The images were carried out at the Brookhouse Institute for Materials Research Canadian Centre for Electron Microscopy at McMaster University in Hamilton, Ontario. The images of the nanostructure sample after drying were obtained using a FEI Titan 80-300 Cubed High-Resolution Transmission Electron Microscope equipped with Gatan 866 model spectrometer optics. The samples were dried and held on a copper grid.

2.7 Dynamic Light Scattering

The radii of gyration of the block copolymer were measured in solution using DLS (Brookhaven BI-200SM Research Light Scattering) equipped with 632.8nm He-Ne laser. The measurements were taken at a 90 degree angle relative to the beam pathway the sample. The samples were filtered using Titan 2 HPLC Filters with 0.2 μm regenerated cellulose membranes.

2.8 Small Angle Neutral Scattering

The SANS experiments were carried out on the NG3 30-m Small Angle Neutron Scattering Instrument at the NIST Center for Neutron Research in Gaithersburg, Maryland. The incident wavelength was 6 \AA . Three sample-to-detector distances, 1.00, 6.00 and 13.00m, were employed, covering a Q-range 0.003 to 0.40 \AA^{-1} the samples were loaded in quartz cells. The sample aperture was 10 \times 10 mm. the experiment was carried out using hydrogenated polymer in deuterated water as the solvent to maximize the contrast. The Scattering pattern was reduced and analysed using the Igro Macros package developed by the NIST center for neutron research, NIST[14].

3 RESULTS AND DISCUSSION

3.1 Fabrication of polypyrrole within SMA templates

The self-assembly of amphiphilic alternating copolymer SMA was studied by Maladier-Jugroot et al. [15]. In particular, eight chains of SMA form stable nanotubes at pH 7 through H-bonding, π - π and π -cation interactions. When immersed in the template system, pyrrole molecules polymerise in the hydrophobic cavity, with no external inductions. The advantages of this synthesis are that the reaction occurs spontaneously in aqueous solution with controlled manner, and it can be applied directly without further processing.

UV-vis spectra were taken during the polymerization in the nanotemplate at various time frames (figure 1). The solutions show a growing shoulder 310 nm at first and a red shift to 480 nm after a week. This shoulder growth is indicative of synthesized polypyrrole within the template [16].

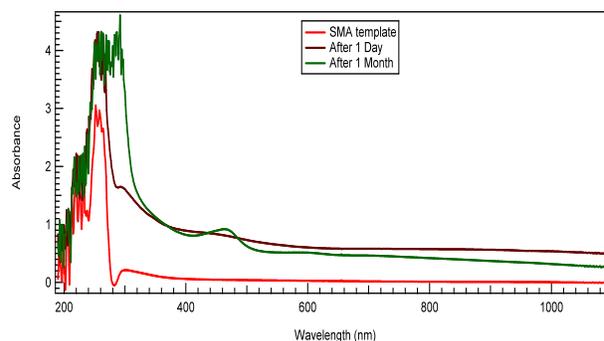


Figure 1: UV spectra of pyrrole addition to SMA solution. The purple and dark blue lines show one day and one month after pyrrole addition respectively.

The IR spectrometry was performed to confirm the previous theoretical prediction of polypyrrole reaction mechanism [1]. It was shown that water has an important role in activation process, it facilitates proton transfer from N to C_{β} of the pyrrole monomers, therefore a CH_2 stretch should be seen on beta carbon. To eliminate the interference of CH_2 from SMA templates, the pH dependent templates were removed by adding HCl or NaOH. The characteristic peaks of SMA were labeled by red boxes. It is clear that all these peaks were present in the blue spectrum (SMA templates) and were missing in the acid/base treated samples. Moreover, both treated samples show peaks at 3428-3410 cm^{-1} and 1564 cm^{-1} corresponding to the N-H stretch and N-H bending in polypyrrole respectively, showing that polypyrrole was synthesized [17-19]. Finally, the CH_2 stretch was shown near 1445 cm^{-1} in both treated samples,

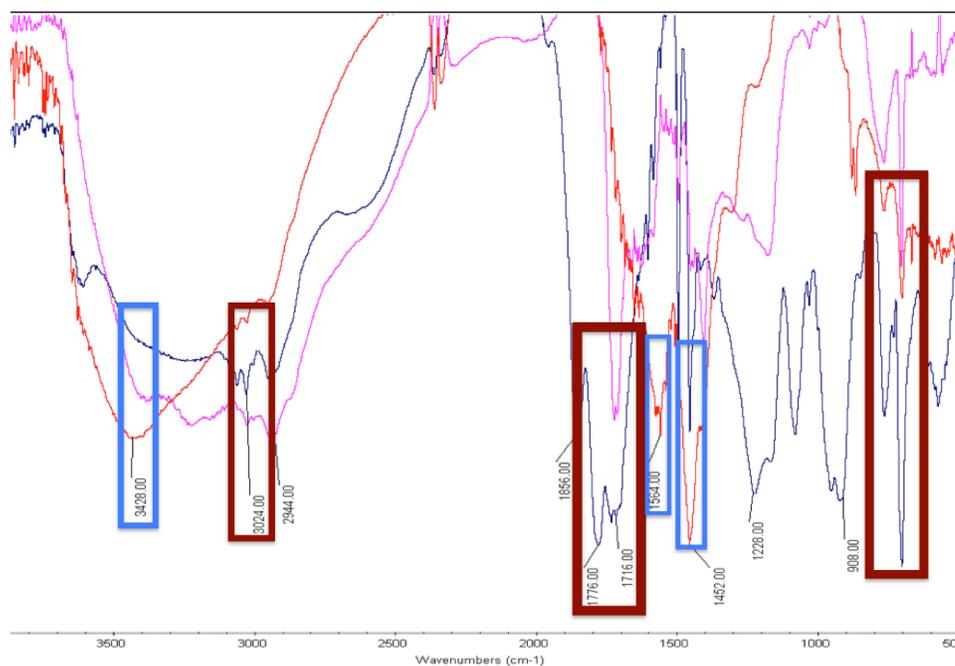


Figure 2: IR spectra for polypyrrole fabrication within SMA template. Blue spectrum: SMA sample. Red spectrum: Base treated sample; Pink spectrum: Acid treated sample.

which is in agreement with the previous simulations where the polymerization is activated at beta-carbon by water and protonated the beta-carbon (CH_2). It is also noteworthy that when the sample was treated with acid, there were still some traces of SMA in the IR spectra and the polypyrrole peaks are also weaker and less sharp compare with the base treated samples (shown in pink spectrum). This phenomenon was due to the fact that SMA is less soluble in acid, therefore when acid was used to remove the template, some SMA copolymers were precipitated out along with the polypyrrole.

3.2 Confinement Effect

Previous study showed that both water and confinement effect have potential impacts on PPY polymerization process [1]. To examine the influence of confinement only, block copolymer (Polystyrene-*b*-poly(acrylic acid)) was selected so that the chemistry between the template and the pyrrole molecules in the hydrophobic cavity would remain the same. In addition, the reaction was carried out in water so that the only criteria changed was the dimension of the cavity.

Sample	THF content	Water content	$2R_h$
21	0.1 wt. %	97%	~125 nm
22	0.1 wt. %	90%	~176 nm
23	0.5 wt. %	90%	~200 nm

Table 1: hydrodynamic radius R_h determined by Dynamic Light Scattering (DLS)

It has been well documented that when amphiphilic diblock copolymers are dissolved in a solvent that is selective for one of the blocks, colloidal aggregates or micelles are formed [20,21]. With that in mind,

tetrahydrofuran THF was used as the common solvent for both blocks, and by adding PAA selective solvent water, polystyrene segments will segregate into a hydrophobic core. Various morphologies/sizes can be found for PS-*b*-PAA micelles depending on the solvent concentration, polymer length and so on. Therefore three samples were prepare with different THF content and water concentration to achieve more diverse morphologies/sizes.

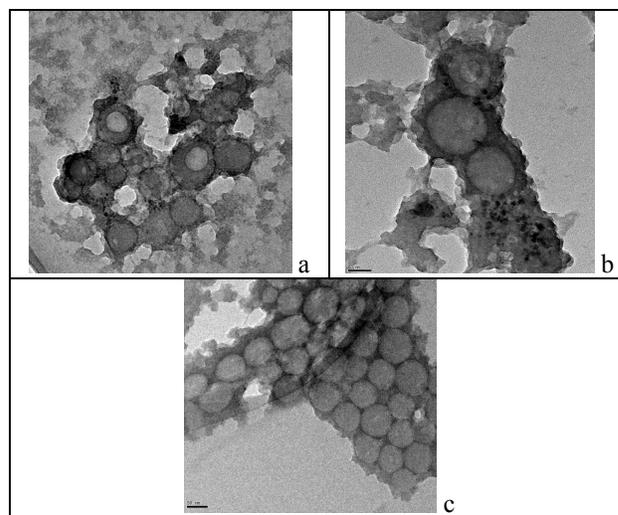


Figure 3: TEM images for PS-*b*-PAA. a, sample 21; b, sample 22; c, sample 23. scale bar=50nm

Dynamic Light Scattering was performed to first obtain the particle size. Table 1 shows the hydrodynamic radii R_h for three samples as 125nm, 175nm and 200nm.

Consequently transmission electron spectroscopy was taken to confirm the size and the presence of polypyrrole within micelles. (Figure 2).

TEM image shows all three samples as uniform spherical micelles formed in water solution and the diameter is around 80nm. The discrepancies between TEM results and DLS results could be due to the average value obtained by DLS measurements show the hydrodynamic diameter ($2R_h$) and refers to how a particle diffuses within a fluid, therefore it is possible that the observed diameter is the aggregation of individual particles.

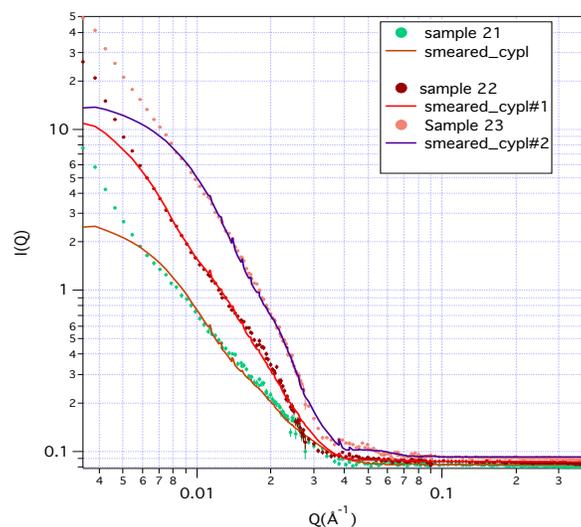


Figure 4: SANS analysis of sample 21, 22 and 23 fitted to form factor cylinder polylenth

	radius (Å)	length (Å)	SLD cylinder (Å ⁻²)	SLD solvent (Å ⁻²)
Sample 21	311.2	107.2	4.2e-06	6.3e-06
Sample 22	448.5	145.3	3.9e-06	6.3e-06
Sample 23	279.3	161.4	4.7e-06	6.3e-06

Table 2: Fitting results from SANS analysis

SANS measurements were done to obtain quantitative information on the structure, size, shape, and internal structure of these micelles in aqueous solution. The samples were prepared in deuterated water (D_2O) with hydrogenated polymers. Figure 4 shows the scattering curves for three samples. Solid lines in the figure is fitting by smeared cylinder polylenth form factor with Q range [0.06, 0.2 Å]. The fitting results are summarized in table 2. The radii are consistant with the TEM results, however it is noteworthy that the radii are much bigger than the lengths of the cylinders, implying that the mophologies for these particles are disc like. Moreover, below Q value 0.06 Å, the fitting curves show less dependency to the scattering pattern meaning that the particles associate into cluster at bigger scale, which supports the bigger dimensions shown in DLS measurements. Therefore we could conclude that the size of the particles are around 80nm in diamer and they are in spherical/disk like shapes.

To examine if polypyrrole was synthesized in the bigger cavity, pyrrole monomer was added to the solution and left to react at room temperature without any disturbance. UV-vis was performed in the same fashion with various time frames (Figure 5). The result shows red shift as the time progresses, however, there is no indicative peaks for polypyrrole oligomers. That is to say, polypyrrole was not synthesized in this scale.

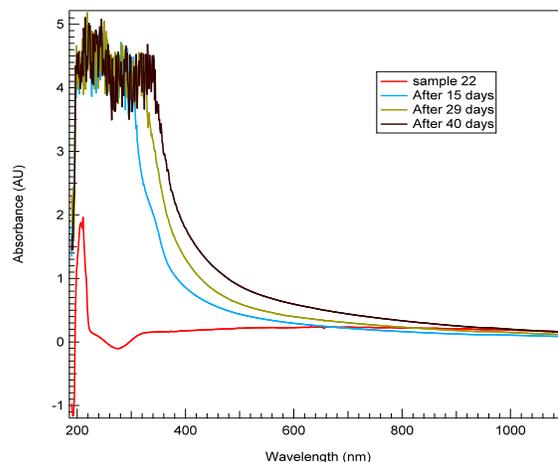


Figure 5: UV-Vis absorbance after pyrrole added to PS-b-PAA templates.

4 CONCLUSION

In conclusion, this work uses characterization techniques such as UV-vis, IR to confirm that polypyrrole was successfully synthesized in the confined SMA templates. Furthermore, using block copolymer PS-b-PAA provide a bigger cavity for templating. The cavity size was analyzed by TEM, DLS and SANS techniques. And Finally there is not indication that polypyrrole was produced in bigger dimension templates.

REFERENCES

- [1] X. Li, *et. al.* Molecular Simulation, in press, 2011. DOI: 10.1080/08927022.2011.563303.
- [2] H. Liu, *et. al.* *Nano Lett.*, **2004**, 4 (4), pp 671
- [3] Allen, B. L. *et. al.* *Adv. Mater.* **2007**, 19, 1439.
- [4] J. Roncali. *Chem. Rev.*, 1992, 92, 711
- [5] I. M. Pumera *et al.* *Chem.-Eur. J.* **2007**, 13, 7644
- [6] P. M. George *et al.* *M. Biomaterials* **2005** 26, 3511.
- [7] D. Munoz-Rojas *et al.* *Small* **2008**, 4, 1301.
- [8] R. Gangopadhyay, A. De, *Chem. Mater.* **12(2006)**
- [9] A.S.W. Chan, *et al.* Molecular Simulation in press, **2010**
- [10] C. Malardier-Jugroot, *et. al.*, *Langmuir*, **2005**, 21(22), 10179.
- [11] A.S.W. Chan, *et. al.* Molecular Simulation, accepted for publication, **2009**
- [12] Malardier-Jugroot, *et al.* *Journal of Physical Chemistry B*, 109(15), 7022 (2005).
- [13] G. Hummer, *et. al.* *Nature*, **2001**, 414, 188
- [14] A. Guinier, *et. al.*, Small angle scattering of X-Rays, John Wiley and Sons, New York, 1955.
- [15] C. Malardier-Jugroot *et al.* *Mol. Simul* 2005; 31(2-3):173-8
- [16] M. Can *et al.* *polymer* 450 (2004) 7011-7016 400
- [17] S. V. Kasisomayajula *et al.* *J. Coat. Technol. Res.*, 7 (2)145.2010.
- [18] H. V.R. Dias *et al.* *Polymer* 47 (2006) 7349.
- [19] K.S. Jang *et al.* *Synthetic Metals* 143 (2004) 289.
- [20] L. Zhang, *et.al.*, *J. Am. Chem. Soc.* 118 (1996) 3168
- [21] Y. Yu, L. Zhang, A. Eisenberg, *Macromolecules* 31 (1998) 114