Facile preparation of polymer nanotube using self-assemblied metal nanotube as sacrificial template

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Abstract. Polymer nanotube (PNT) is a polymer nanomaterial with tubular structure. In this study, we have developed a simple technique for the fabrication of polymer nanotubes by using self-assembled metal organic nanotube (MONT) as a sacrificial template and dendritic amine and acid as precursor molecules. MONT was firstly prepared by the self-assembly of amphiphilic molecule **1** with copper(II) nitrate in methanol. And then, a dendritic amine [tris(2-aminoethyl) amine, tris-amine] was added to a dispersion of MONT in THF. A coating layer of the tris-amine formed on the surface of MONT. The coating layer on the nanotube surface was further cross-linked by an active ester of citric acid. Finally, the self-assemblied template was easily removed in hot ethanol and the PNTs were obtained by filtration. The results showed that the cross-linked polymers form PNTs up to 80% when the amount of the tris-amine is 0.4 molar equivalent of MONT. The lengths of PNTs are about 500nm~3μm, inner diameters are 60 ~ 100 nm and outer diameters are 80 ~ 120 nm.

Introduction

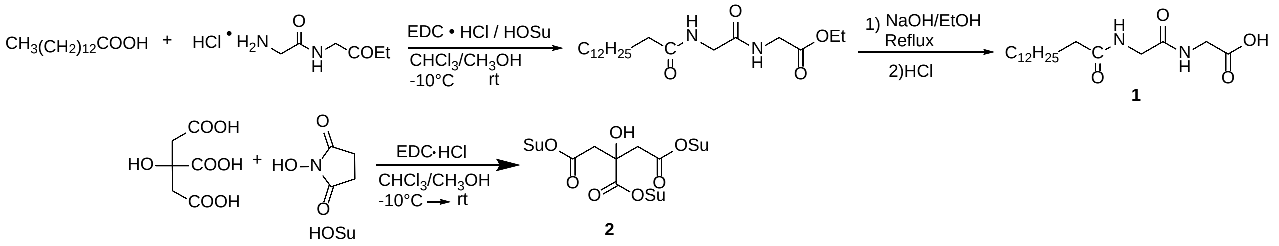
Polymer nanotubes (PNTs) have attracted considerable attention due to their diverse applications, ranging from controlled drug delivery to biotechnologies [1-5]. Template method is an important and effective method for preparation of special structural and functional nanomaterials[6-8]. By using template method, the unique structure, morphology and function of materials can be controlled by the expected design, and good template is the key to preparation of special functional materials [9-13].

Self-assembled metal organic nanotube (MONT) is a hollow tubular material, prepared by self-assembly of amphiphilic molecules and metal ions [14]. MONT is a good template potential for the preparation of PNT because of simple preparation process and cheap raw materials. Shimizu group reported several MONT systems prepared by adding metal ions into the self-assembling system of amphiphilic molecules with different carbon chains [15-18]. The MONTs with various metal ions on the surface were successfully obtained. They subsequently reported the preparations of CuO and Mn_2O_3 nanotubes using MONTs covered with copper ions as a template [19]. Since the interactions among self-assembly molecules are weak, the structures of MONTs ere easily able to be destroyed at high temperature, strong acid, alkali condition, or even in some organic solvents. Therefore, the preparations of PNTs using MONTs as the template have an practical significance.

In this paper, we will report a simple process for the preparation of PNT by using MONT as a template and dendritic amine and acid as the precursor molecules.

Results and discussion

*Synthesis of the amphiphilic molecule **1*** [19]: As shown in Scheme 1, a solution of EDC•HCl in $CHCl_3$ was added a solution of myristic acid and HOSu in $CHCl_3$ with stirring at -10 °C. After the mixture was stirred at 0 °C for 1 h, a solution of ethyl glycylglycinate hydrochloride in $CHCl_3$ and triethylamine was added to the reaction mixture. The mixture was stirred for another 1 h at 0 °C and overnight at room temperature. The reaction mixture was washed with 10% citric acid, 4% $NaHCO_3$, brine and water, dried over anhydrous $MgSO_4$, filtered and evaporated under reduced pressure to give a white powder. The powder product was subjected to alkali hydrolysis and acidification in ethanol to give a white precipitate. The white precipitate was filtered, washed and dried in vacuum. The amphiphilic molecule **1** was obtained as a white powder in 93.6% yield. m.p. 168.4 ~ 170.0°C; ^1H NMR (500 MHz, DMSO-d_6) δ 12.59 (s, 1H), 8.07 (s, 1H), 8.03 (s, 1H), 3.86~3.59 (m, 4H), 2.12 (s, 2H), 1.49 (s, 2H), 1.25 (s,20H), 0.86 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 172.98, 171.59, 169.86, 42.21, 41.12, 40.47, 40.30, 35.67,31.76, 29.53, 29.50, 29.48, 29.40, 29.29, 29.17, 25.57, 22.55, 14.40; IR (kBr) v: 3291, 3082, 2915, 1725, 1608,1559, 1462, 1420, 1274, 720 cm^{-1}; [M＋1]＝343.3.



Scheme 1. Preparations of amphiphilic molecule **1** and active ester **2**

Synthesis of active ester of citric acid ***2*** [20]: As shown in Scheme 1, a solution of EDC•HCl in $CHCl_3$ was dropped into a solution of citric acid and HOSu in $CHCl_3/CH_3OH$ at -10 °C. After addition, the mixture was stirred for 1h at 0 °C and overnight at room temperature. The reaction mixture was washed with 10% citric acid, 4% $NaHCO_3$, brine, and water. The organic layer was dried over anhydrous $MgSO_4$, filtered and evaporated under reduced pressure to give colorless oil in 25.6% yield.

Preparation of MONT: MONT was prepared by the self-assembly of **1** with $Cu(NO_3)_2$ in methanol/water at room temperature [19]. The tubular structures were confirmed by scanning electron microscope (SEM) and scanning transmission electron microscopy (STEM), as shown in Fig. 1. The self-assemblied MONTs have the lengths from hundreds of nanometers to several micrometers and most of tubes have the lengths of 800 nm ~ 3 μm. Outer diameters are 60 ~100 nm, inner diameters are 20 ~ 30 nm and wall thicknesses are 20 ~ 40nm.

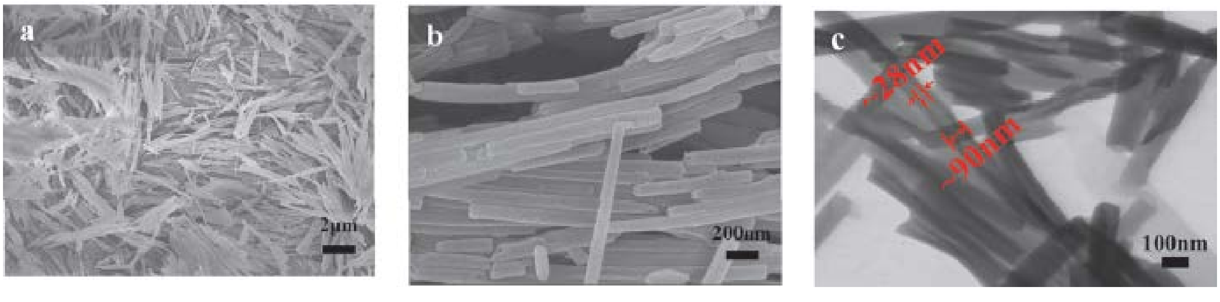


Fig. 1. SEM (a, b) and STEM (c) images of MONT

Preparation of PNT: Since Cu^{2+} as a transition metal ion has good coordination ability, the MONT covered with Cu^{2+} on the surface is a potential template by forming Cu(II)-complex. Dendritic tris(2-aminoethyl) amine (tris-amine) formed a complex layer with Cu^{2+} ions on the surface of MONT, and then a cross-linked reaction was carried out by a coupling reaction with the dendritic active ester **2** to form a stable polymer layer on MONT surface. Finally, PNTs were obtained by dissolving the self-assemblied template in hot ethanol and subsequent heat filtration. The preparation process for PNT is shown in Fig. 2.

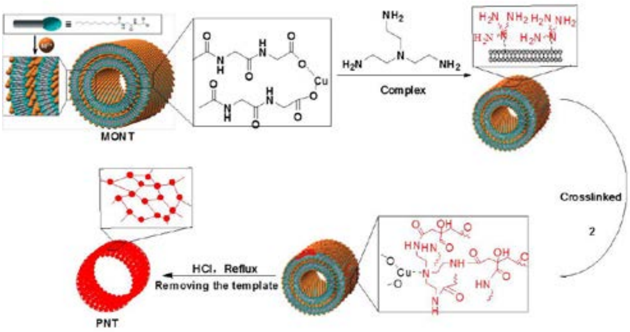


Fig. 2. Schematic process for PNT preparation

Table 1. Molar ratio of tris-amine and active ester **2** to MONT (0.2 mmol)

Enter	Tris-amine	**2**	TFP	Product
1	0.1 eq.	0.1 eq.	~ 10%	PNT 1
2	0.2 eq.	0.2 eq.	~ 20%	PNT 2
3	0.3 eq.	0.3 eq.	~ 50%	PNT 3
4	0.4 eq.	0.4 eq.	~ 80%	PNT 4
5	0.5 eq.	0.5 eq.	~ 70%	PNT 5

In order to improve the tube-forming percentage (TFP), the ratios of tris-amine to MONT were screened. The surface morphologies and TFPs (visual, the same below) of PNTs 1~5 were characterized by SEM images. The results were summarized in Table 1. According to SEM images of PNTs 1~5, we found when the amount of tris-amine was 0.4 molar equivalent of MONT, the highest TFP was obtained. The structures and diameter distributions of PNT 4 were further characterized by STEM. The SEM and STEM images of PNT 4 are shown in Fig. 3. The lengths of PNT 4 are about 500 nm ~ 3 μm, outer diameters are 80 ~120 nm and inner diameters are 60 ~ 100 nm.

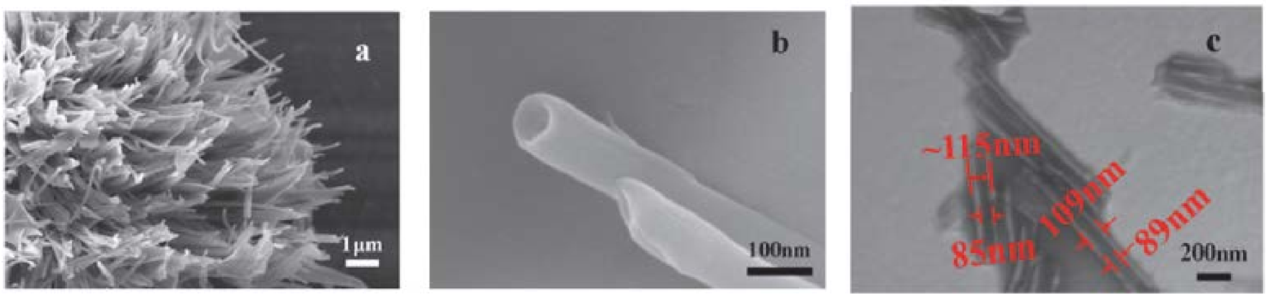


Fig. 3. SEM and STEM images of PNT 4

When the amounts of tris-amine were 0.1 ~ 0.3 molar equivalent of MONT, TFPs of PNTs 1~3 were low, 10%, 20% and 50% respectively, and a lot of sheet-like structures were found. The inadequate tris-amines sparsely distributed on the surface of the template. Therefore, there should be many large vacant spaces bigger than the size of ester **2**, which resulted in many uncoupling areas during cross-linked process. After removal of the internal template, the cross-linking layers would be discontinuous in these uncoupling areas, which is the reason that a lot of sheet-like structures form. With the increases of tris-amine/MONT mole ratio, the TFPs of PNTs gradually increased. When the amount of tris-amine was 0.4 molar equivalent of MONT, up to 80% cross-linked polymer products formed PNT. At this molar ratio, the tris-amine was able to evenly form moderately wrapped layer on the surface of MONT, and then formed a homogeneous polymer layer surrounding the tube after cross-linked reaction. The PNTs with uniform lengths and diameters could be obtained after removal of the internal template. When the amount of tris-amine was 0.5 molar equivalent of MONT, the TFP slightly decreased to about 70%. The sufficient tris-amine completely wrapped the surface of MONT even freely remained in the solvent. The amino groups of free tris-amine reacted with **2** to generate breakpoints, which reduced the cross-linked probability on the surface of MONT, leading to the decrease of TFP.

For determining the compositions and structures of MONT and PNT, the MONT and PNT were characterized by differential scanning calorimetry (DSC) and X-ray diffraction (XRD). In the DSC curves of MONT, as shown in Fig. 4a, there is a broad peak between 70 ~ 120ºC, which is heat absorption for destroying self-assembled structures, including the van der Waals forces, hydrogen bondings and other intermolecular forces. The peak at 210ºC probably means the heat decomposition of the copper salt of amphiphilic molecule **1**. Further increasing the temperature will lead to the carbonization of the decomposed organic compounds, which give peaks higher than 220 °C. Different from the MONT, there is no any heat absorption peak in the temperature below 150 °C in DSC curve of PNT, indicating no self-assembled forces for PNT. With the temperature up to 170 °C, the PNT curve displays a high sharp peak because the sample probably occurs to absorb heat to melt. When the temperature rises to 220 °C, the PNT curve shows an absorption peak because of the decomposition even carbonization of polymers. Through the analyses of the DSC curves for MONT and PNT, we confirm that PNT has a higher thermal stability than self-assemblied MONT.

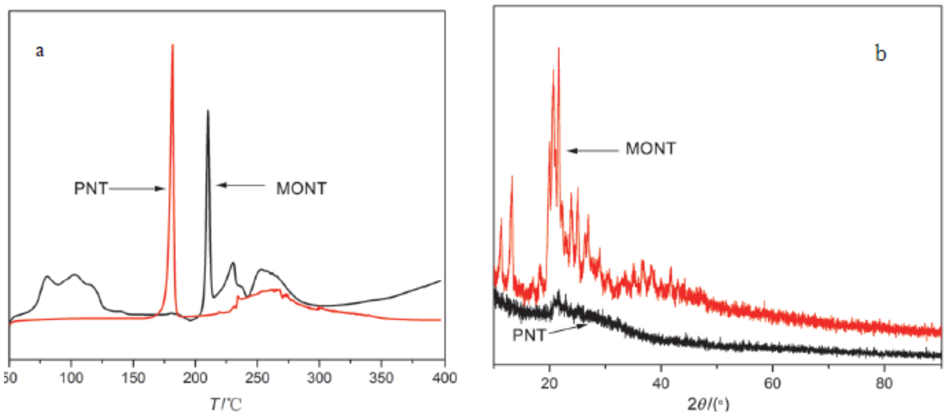


Fig. 4. DSC(a) and XRD(b) curves of MONT and PNT

In the XRD curves of MONT and PNT(shown in Fig. 4b), we easily find the Cu^{2+} characteristic peaks in MONT curve, which proves the existence of copper ion complexes in MONT. Conversely, only very weak peaks of Cu^{2+} are able to be observed in PNT curve, indicating most of MONT template successfully removed. The trace of Cu^{2+} comes from two possible ways: one is a trace of template unsuccessfully removed; the other is a trace of residual carboxyl groups from citric acid combining with copper ions in the process for removing the template.

Conclusion

We have developed a simple process for the preparation of PNT by using MONT as a template and dendritic amine and acid as precursor molecules. A dendritic amine firstly coordinates with copper ions on the surface of template, and then forms a coating layer on the surface of MONT. The coating layer is further cross-linked by an active ester of dendritic acid. Finally, the self-assembled template is removed and the PNT is successfully obtained. The PNT were characterized by SEM, STEM, DSC and XRD. The results show that when the amount of tris-amine is 0.4 molar equivalent of MONT, up to 80% cross-linked products form PNT. The lengths of PNTs are about 500nm ~ 3μm, inner diameters are 80 ~ 100 nm and outer diameters are 100 ~ 125 nm. Next, we will further explore the chemical modification of PNT and its application as a drug carrier.

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