Swollen liquid crystals as soft and structure directing templates to synthesize polyindole nanostructures having distinctive electrochemical properties

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Abstract

Using swollen liquid crystals (SLCs) as a soft template, different Polyindole (PIn) nanostructures having different morphology have been synthesized successfully at different temperatures. SLCs containing indole ring was formed by a quaternary system containing cetyltrimethyl-ammonium bromide (CTAB) or sodium dodecyl sulfate (SDS) as a surfactant, brine, indole: cyclohexane mixture as oil phase and 1-pentanol as co-surfactant. The indole containing mesophases were polymerized using ammonium persul fate as an oxidant and further nanocomposites were extracted from the mesophases. Finally the extracted and processed samples were characterized using different spectroscopic techniques. The electrochemical properties of PIn nanostructures were also investigated using cyclic voltammetry.

Keywords: Polyindole, liquid crystals, polymers, nano-structures

1. Introduction

In the last few decades, large number of conducting polymers like polypyrrole [1], polyaniline [2], polyazulene [3], polythiophene [4], polycarbazole [5], polyphenylene [6], have been synthesized for various applications. Widely explored applications of different conducting polymers and their derivatives, makes them very interesting materials. Specially indole based conducting polymer research have earn lots of attention due to their wide applications in a variety of field such as smart biomaterials [8], bio interface materials, sensors, actuators, anti-corrosion, supercapacitors [10] etc. Among them indole based fused ring conjugated polymer system such as polyindole (PIn) is meticulous due to its excellent thermal stability, high redox activity, slow rate of degradation in comparison with other conducting polymers [11-13]. The PIn has gained enormous attention in different research domains, such as organic electronics [14], electro-catalysis/catalysis [15, 16], batteries [17], anticorrosion coatings [18], sensors [19] etc. Chemical and electrochemical methods are the two basic routes for PIn synthesis. Chemical polymerization routes can be emulsion polymerization, interfacial polymerization [20, 21] microwave assisted polymerization [22] etc. Different oxidizing agents such as FeCl₃, Cu(ClO₄)₂·6H₂O, KIO₃, (NH₄)₃S₂O₃, H₂O₂ etc. were used for chemical oxidation of indole. In electrochemical method of polymerization, the deposition of PIn usually takes place on working electrode [23]. Moreover, during either chemical or electrochemical methods for PIn synthesis, the polymerization of indole takes place only at 2,3-position and benzene ring as well as nitrogen atoms are not involved in the polymerization process [24-26].

Depend upon synthetic route used to achieve these polymers they have different nanostructures. Nanostructures have significant impact on its properties. Different applications required different kind of structural properties such as electroactive materials [27, 28], materials for waste water treatment [29], energy storage applications [30] etc. requires different structural properties. The different synthetic methods are available for controlling nanostructure of materials such as hard templates [31], soft templates [32], electrochemical oxidation [33], and reverse micelle [34] etc. Among all the synthetic methods, Soft template approach is better because template can be removed by simple washing and on the other hand, hard templates approach requires use of harsh condition for template removal and it may rupture the desired nanostructures [35, 36]. Recently the use of swollen liquid crystals (SLCs) as soft and structure...
directing template has garnered greater attention of scientific community for synthesizing different nanostructures of metals, polymers and nanocomposites \(^{37}\). SLCs can be formed by a quaternary mixture of water, oil, surfactant and co-surfactant \(^{38}\). So the main task for the use of SLCs as soft and structure directing template for different PIn nanostructures synthesis is still an unexplored area of research and here we investigate first time that different PIn nanostructures can be synthesized by using SLCs. Spherical PIn nanostructure were formed by vortex mixing of oxidizing agent (ammonium persulfate) while rod shape morphology was obtained by slow diffusion of oxidant in indole containing mesophase. The present study demonstrates the easy and one pot method of synthesis for different PIn nanostructures by just tuning the way of oxidant mixing for indole polymerization. So the main task for the use of SLCs as soft and structure directing template for different PIn nanostructures synthesis is still an unexplored area of research and here we investigate first time that different PIn nanostructures can be synthesized by using SLCs. Spherical PIn nanostructure were formed by vortex mixing of oxidizing agent (ammonium persulfate) while rod shape morphology was obtained by slow diffusion of oxidant in indole containing mesophase. The present study demonstrates the easy and one pot method of synthesis for different PIn nanostructures by just tuning the way of oxidant mixing for indole polymerization.

2. Materials and Methods

2.1 Materials
Indole, ammonium persulfate (APS), dimethyl sulfoxide (DMSO), sodium dodecyl sulphate (SDS) were purchased from Himedia, sodium chloride, cyclohexane, 1-pentanol from RANKEM, toluene, acetonitrile (ACN), deuterated chloroform (CDCl₃) form Sigma-Aldrich have been used as received without any further purification.

2.2 Synthesis of Polyindole (PIn)
PIn was synthesized by oxidation of indole using APS as oxidizing agent in presence of SLCs as structure directing agent. The indole containing SLCs were synthesized by slightly modifying the already reported procedure for polyaniline synthesis by our research group \(^{39}\). In this synthesis process, indole (1mmol) was first dissolved in the aqueous brine solution (1ml, 0.1M) and then heated up to 50 °C. Further SDS (0.4g) was added in this solution which is followed by the addition of toluene (350µl) as oil phase. SLCs were formed by adding 1-pentanol as co-surfactant in desired amount with intermittent vortex mixing. The indole containing mesophase was kept undisturbed for few days and then APS as oxidizing agent (1mmol) was added at 5 °C under different polymerization conditions i.e. under slow polymerization (diffusion, D), where the APS was poured over the mesophase or under fast polymerization conditions (mixed, M), where the APS was added to the mesophase under vortex mixing. The mixture was kept for 24 hours in case of mixing conditions and 48 hours for diffusion conditions for completion of polymerization. The green colour precipitate is formed after completion of polymerization, which was washed 3-4 times with ACN. Finally the precipitate were collected by filtration and dried in hot air oven at 70 °C overnight. The different PIn samples were code-named as PIn-M-5, PIn-D-5, (PIn=Polyindole, M=mixed, D=diffusion, 5=polymerization temperature). To investigate and understand the SLCs template confinement effect on PIn nanostructures with respect to temperature, we also studied the polymerization of indole at 20 ºC and 40 ºC. Synthesized PIn samples at 20 ºC and 40 ºC temperature, here after code named are changed as PIn-D-20, PIn-M-20, PIn-D-40, PIn-M-40 respectively.

2.3 Characterization
The UV-visible spectra of the PIn samples were obtained in DMSO by using Perkin Elmer Lambda-750 spectrophotometer. The FT-IR spectra of samples were recorded on Perkin Elmer FT-IR spectrophotometer using KBr pellet at wavelength range of 400 to 4000cm⁻¹. 1HmmR spectra were recorded by using JEOL RESONANCE ECX-400 in DMSO and the XRD patterns were recorded on Bruker-D8-Advance X-ray diffractometer in 20 (°) range of 5-80° using Cu Kα (λ = 1.5405 Å). In this work, elemental analysis was also done by using XPS (X-ray Photoelectron spectrometer, Kratos, Axiz Ultra DLD) and spectrum was recorded using Al Kα as radiation source. Morphology of PIn samples was further investigated by using FE-SEM (Carl Zeiss Ultra Plus). TGA analysis was performed at the temperature range of 25-1000 ºC with heating rate of 10 ºC/min under N₂ atmosphere using EXSTAR TG/DTA 6300. The cyclic voltammetry studies were carried out in 0.1N H₂SO₄ with different scan rates in a potential range of -0.3 to 0.4 V using saturated calomel electrode (SCE) as reference, glassy carbon (GC) as working and Pt-wire as counter electrode.

3. Results and Discussion
When cyclohexane was mixed with the aqueous brine solution of indole and SDS, a white emulsion was formed, which was further transformed into transparent and colorless gel by the addition of 1-pentanol as co-surfactant. The appearance of transparent and colorless mesophase confirmed the formation of SLCs \(^{40}\). After the formation of mesophase, solid APS as oxidizing agent was added under different reaction conditions. When the solid APS was just added into the indole containing mesophase from the top, the green colour starts to appear at the interface of oxidant and indole under diffused condition. The width of the colored band slowly increased from top to bottom (slow polymerization step) at the interface. On the other hand, under vortex mixing condition, the mesophase was suddenly changed from colorless to dark green color at 5 ºC (fast polymerization step). The mixture was further kept for 24 hours in case of mixing condition and 48 hours in case of diffused conditions for completion of polymerization. Similarly, the experiment was repeated at 20 ºC and 40 ºC to further investigate the control over morphology at different temperatures. After completion of polymerization, product was further washed with ACN to remove unreacted indole and APS. Thoroughly washed samples were characterized using different characterization techniques.

3.1 Physico-chemical characterization
Preliminary characterizations of PIn nanostructures have been carried out by recording UV-Vis spectra and the results obtained are shown in figure 1. UV-Vis spectra of PIn samples are recorded in water. It shows the characteristic absorption peaks at 278nm and at 322nm. These peaks ascribed to n → π* transitions observed for PIn \(^{41}\).
The FT-IR spectra of all Pln samples, it shows a broad band at 3400cm⁻¹ (N-H stretching band), 1567cm⁻¹ (N-H deformation band) and 735cm⁻¹ (out of plane deformation of benzene). The presence of N-H stretching, the N-H deformation and out of plane deformation of benzene implies that the polymerization does not take place at benzene ring and nitrogen species while the preferable sites for polymerizations are 2 and 3 (different sites are indicated in figure 3) [42, 43]. The other bands also appeared as 1593cm⁻¹ (C-C stretching vibrations of indole unit), 1453cm⁻¹ and 1370cm⁻¹ (stretching frequency of aromatic C-N and C=N), 1199cm⁻¹ and 1047cm⁻¹ and (S=O stretching bands). By the above FT-IR spectra the Pln formation using SLCs is also confirmed.

In addition to UV-Vis and FT-IR spectra, the formation of Pln is also confirmed by ¹HnmR, which is shown in figure 3. The ¹HnmR characteristics data of Benzene ring of indole is given as δ= 9.06 ppm for H4, δ= 6.64-7.72 ppm for H5, δ= 6.7-7.71 ppm for H6, δ= 7.72-7.85 ppm for H7[44]. Due to the influence of H7 proton of benzene ring, the peak for N-H is shifted from 10.74 ppm to 11.03 ppm [45].
In order to understand the planes of synthesized PIn, the XRD pattern of PIn samples has been recorded and represented in figure 4. It shows that one broad diffraction peak at $2\theta=18^\circ$ and other at $2\theta=25^\circ$ is due to reflection of the polymer backbone $^{[46]}$. Sharp peak at $25^\circ$ depicted slightly crystalline nature of synthesized polyindole samples, while at $18^\circ$ confirms amorphous nature of polyindole $^{[47]}$.

**Fig 4:** XRD pattern of PIn samples: (a) PIn-5M (b) PIn-5D (c) PIn-20M (d) PIn-20D (e) PIn-40M (f) PIn-40D.

The elemental analyses of synthesized PIn samples (PIn-20M) were carried out by using XPS as shown in figure 5 (a), (b) and (c). The presence of C, O, N and S has been confirmed from XPS spectra as shown in figure 5 (a). The elemental shoulders of S and O are appearing due to remaining content of APS and moisture content. Moreover, the presence of C$_{1s}$ and N$_{1s}$ shoulders around 284.68 eV and 400.2 eV in the XPS spectrum of PIn confirm the polymerization of indole $^{[48]}$.

**Fig 5:** XPS spectra of synthesized PIn samples (a) Survey scan, (b) C$_{1s}$ scan and (c) N$_{1s}$ scan.

The thermal stability of PIn sample (PIn-20M) was investigated by using TGA under N$_2$ atmosphere as shown in figure 6. The decomposition of PIn sample in the temperature range from 100-200 °C is due to the loss of trapped moisture content as well as the presence of oligo-indole residues $^{[49]}$. In addition, the surfactant i.e. SDS present in the sample start to degrade at the temperature range of 200-300 °C $^{[50]}$. Moreover, as the temperature rises, the degradation of PIn skeletal backbone started above 400 °C $^{[51]}$. 

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FESEM images of different PIn samples synthesized by using SLCs under mixed and diffused conditions at 5, 20 and 40 °C are shown in figure 7. The PIn samples under diffused conditions at 5 and 20 °C (figure 7 a and c) showed rod-like nanostructures, whereas, PPy synthesized under mixed conditions (figure 7 b and d) but at similar temperature conditions showed spherical morphology. The difference in the morphology of PPy may be attributed to the difference in the rate of polymerization during mixed and diffused conditions. Our previous investigations explained well that under diffusion conditions the rate of polymerization is slow and under mixed conditions the rate of polymerization is fast. \cite{52} Thus due to difference in the rate of polymerization, the difference in PIn nanostructures morphology is also observed. Here, we also investigated that the SLCs confinement effect is dominating only up to 20 °C.

To further verify this observation, the SLCs assisted polymerization was studied at 40 °C. The polymerization at 40 °C under both conditions yields nanostructures of same morphology i.e. spherical nanostructures. It may be attributed due to the fact that the polymerization using APS is exothermic and due to high temperature conditions, as well as exothermic nature of the reaction. The meso phase becomes unstable in both the cases i.e. under mixed and diffusion conditions. Thus, the SLCs mesophase confinement effect on controlling the nanostructures morphology is absent diffusion conditions as well.

Electrochemical activity of PIn samples were also studied using CV which is recorded at different scan rates at 0.1N H2SO4 as electrolyte as shown in figure 8.
The equation (1) is used for calculation of gravimetric specific electrochemical capacitance ($C_{sp}$) and given as:

$$C_{sp} = \frac{\int I dV}{\nu m V}$$

(1)

Where, $I$ represents the response current, $V$ signifies the potential window ($V$), $\nu$ indicates the potential scan rate ($mV \cdot s^{-1}$) and $m$ stands for the mass of the active material in the electrode. The calculated specific capacitance ($C_{sp}$) of all PIn samples are given in table 1 (supporting).

The maximum specific capacitance ($C_{sp}$) of 260.41 F-g$^{-1}$ was estimated at 1 mV-s$^{-1}$ for PIn-40D. Specific capacitance of PIn samples gradually decreases with increase in the scan rate due to insufficient ion electrode interaction at high scan rate.

4. Conclusions
Using SLCs as ‘soft’ templates at different temperatures can easily control PIn nanostructures morphology. In this work, spherical morphology of PIn nanostructures were obtained under vortex mixing conditions and rod like structures were obtained under diffusion conditions, which was thoroughly studies under different spectroscopic techniques. The synthesized nanostructures under different synthetic conditions also showed the difference in their maximum specific capacitance ($C_{sp}$).

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6. References

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