



Swollen Liquid Crystals as Soft and Structure Directing Templates for the Synthesis of Polyindole

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Using swollen liquid crystals (SLCs) as a soft template, different polyindole nanostructures having different morphology have been synthesized successfully at different temperatures. The 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 persulfate 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 polyindole nanostructures were also investigated using cyclic voltammetry.

Keywords: Polyindole, Liquid crystals, Polymers, Nano-structures, Mesophase.

INTRODUCTION

In last few decades, large number of conducting polymers like polypyrrole [1], polyaniline [2], polyazulene [3], polythiophene [4], polycarbazole [5], polyphenylene [6-9] 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 earned lots of attention due to their wide applications in a variety of field such as smart biomaterials [10], biointerface materials [11], actuators, sensors, anti-corrosion, supercapacitors [2], *etc.* Among them indole based fused ring conjugated polymer system such as polyindole is meticulous due to its excellent thermal stability, high redox activity, slow rate of degradation in comparison with other conducting polymers [12-14]. The polyindole has gained enormous attention in different research domains, such as organic electronics [15], electro-catalysis/catalysis [16,17], batteries [18], anticorrosion coatings [19] and sensors [20].

Chemical and electrochemical methods are the two basic routes for polyindole synthesis. The chemical polymerization routes can be emulsion polymerization, interfacial polymeri-

zation [21,22], microwave assisted polymerization [23], *etc.* Different oxidizing agents such as FeCl_3 , $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, KIO_3 , $(\text{NH}_4)_2\text{S}_2\text{O}_8$, H_2O_2 , *etc.* were used for chemical oxidation of indole. In electrochemical method of polymerization, the deposition of polyindole usually takes place on the working electrode [24]. Moreover, during either chemical or electrochemical methods for polyindole 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 [21,25,26].

Depend upon the 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 wastewater 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]. The 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 polyindole nanostructures synthesis is still an unexplored area of research and here we investigate first time that different polyindole nanostructures can be synthesized by using SLCs. Spherical polyindole 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 an easy and one pot method of synthesis for different polyindole nanostructures by just tuning the way of oxidant mixing for indole polymerization.

EXPERIMENTAL

The chemicals and solvents *viz.* indole, ammonium persulfate (APS), dimethyl sulfoxide (DMSO), sodium dodecyl sulphate (SDS) were purchased from Himedia; sodium chloride, cyclohexane, 1-pentanol from RANKEM, toluene, acetonitrile, deuterated chloroform from Sigma-Aldrich and used as received without any further purification.

Synthesis: Polyindole 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 (0.117 g, 1 mmol) was dissolved in the aqueous brine solution (1 mL, 0.1 M) and then heated up to 50 °C. Further, SDS (0.4g) was added in this solution which is followed by the addition of toluene (350 μ L) as oil phase. The SLCs were formed by adding 1-pentanol (300 μ L) as co-surfactant in desired amount with intermittent vortex mixing. The indole containing mesophase was kept undisturbed for 3 days and then APS as oxidizing agent (0.228 g, 1 mmol) was added at 5 °C under different polymerization conditions *i.e.* under slow polymerization (diffusion), where the APS was poured over the mesophase or under fast polymerization conditions (mixed), where the APS was added to the mesophase under vortex mixing. The mixture was kept for 24 h in case of mixing conditions and 48 h for diffusion conditions for completion of polymerization. The green colour precipitate is formed after completion of polymerization, which was washed 3-4 times with acetonitrile. Finally, the precipitate was collected by filtration and dried in hot air oven at 70 °C overnight. The different polyindole samples were coded as: PIn-M-5, PIn-D-5, (where, PIn = polyindole, M = mixed, D = diffusion, 5 = polymerization temperature). To investigate and understand the SLCs template confinement effect on polyindole nanostructures with respect to temperature, the polymerization of indole at 20 °C and 40

°C were also studied. Synthesized polyindole samples at 20 °C and 40 °C, here after code named were changed to PIn-D-20, PIn-M-20, PIn-D-40, PIn-M-40, respectively.

Characterization: The UV-visible spectra of the polyindole samples were obtained in DMSO solvent 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 4000 to 400 cm^{-1} . ^1H NMR 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 2θ (°) range of 5-80° using $\text{CuK}\alpha$ ($\lambda = 1.5405 \text{ \AA}$). The elemental analysis was also done by using XPS (X-ray Photoelectron spectrometer, Kratos, Axix Ultra DLD) and spectrum was recorded using $\text{AlK}\alpha$ as radiation source. Morphology of polyindole samples was further investigated by using FE-SEM (Carl Zeiss Ultra Plus). TGA analysis was performed at the temperature range of 25-1000 °C with heating rate of 10 °C/min under N_2 atmosphere using EXSTAR TG/DTA 6300. The cyclic voltammetry studies were carried out in 0.1N H_2SO_4 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 platinum (Pt) wire as counter electrode.

RESULTS AND DISCUSSION

When cyclohexane was mixed with the aqueous brine solution of indole and sodium dodecyl sulfate (SDS), a white emulsion was formed, which further transformed into the transparent and colourless gel by the addition of 1-pentanol as co-surfactant. The appearance of transparent and colorless mesophase confirmed the formation of the swollen liquid crystals (SLCs) [40]. After the formation of mesophase, 1 mmol of solid ammonium persulfate (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 °C (fast polymerization step). The mixture was further kept for 24 h in case of mixing condition and 48 h in case of diffused conditions for completion of polymerization. Similarly, the experiment was repeated at 20 °C and 40 °C to further investigate the control over morphology at different temperatures. After completion of polymerization, product was further washed with acetonitrile to remove unreacted indole and APS. Thoroughly washed samples were characterized using different characterization techniques.

Preliminary characterizations of polyindole nanostructures have been carried out by recording UV-Vis spectra and the obtained results are shown in Fig. 1. The UV-Vis spectra of polyindole samples were recorded in water. It shows the characteristic absorption peaks at 278 nm and at 322 nm. These peaks ascribed to $n \rightarrow \pi^*$ transitions observed for polyindole [41].

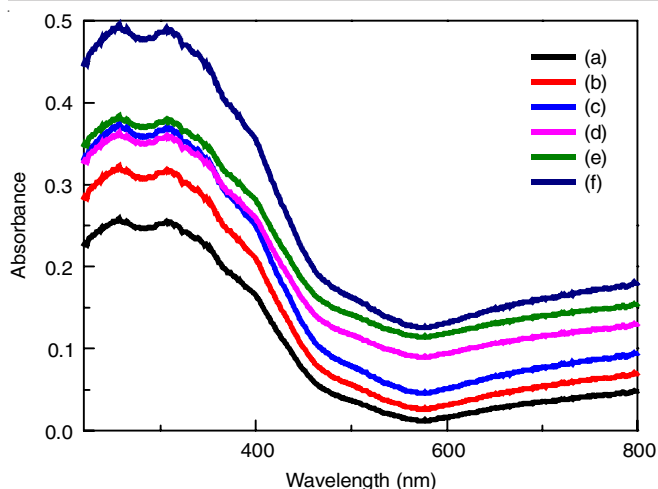


Fig. 1. UV-vis spectra of different polyindole samples in water: (a) PIn-5-M (b) PIn-5-D (c) PIn-20-M (d) PIn-20-D (e) PIn-40-M and (f) PIn-40-D

FT-IR analysis: The FT-IR spectra of all the polyindole samples, it shows a broad band at 3400 cm^{-1} (N-H *str.*), 1567 cm^{-1} (N-H *def.*) and 735 cm^{-1} (out-of-plane *def.* 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 Fig. 2) [42,43]. The other bands also appeared as 1593 cm^{-1} (C-C *str.* vibrations of indole unit), 1453 cm^{-1} and 1370 cm^{-1} (*str.* frequency of aromatic C-N and C=N), 1199 cm^{-1} and 1047 cm^{-1} and (S=O *str.*). By the above FT-IR spectra, the polyindole formation using SLCs is also confirmed.

^1H NMR studies: The ^1H NMR characteristics data of benzene ring of indole is given as $\delta = 9.06\text{ ppm}$ for H4, $\delta = 6.64\text{--}7.72\text{ ppm}$ for H5, $\delta = 6.7\text{--}7.71\text{ ppm}$ for H6, $\delta = 7.72\text{--}7.85\text{ ppm}$ 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].

XRD studies: In order to understand the planes of synthesized polyindole, the XRD pattern of polyindole samples has been recorded and represented in Fig. 3. It shows that one broad diffraction peak at $2\theta = 18^\circ$ and other at $2\theta = 25^\circ$ is due to the reflection of polymer backbone [46]. A sharp peak at 25° depicted slightly crystalline nature of synthesized polyindole samples, while at 18° confirms the amorphous nature of polyindole [43].

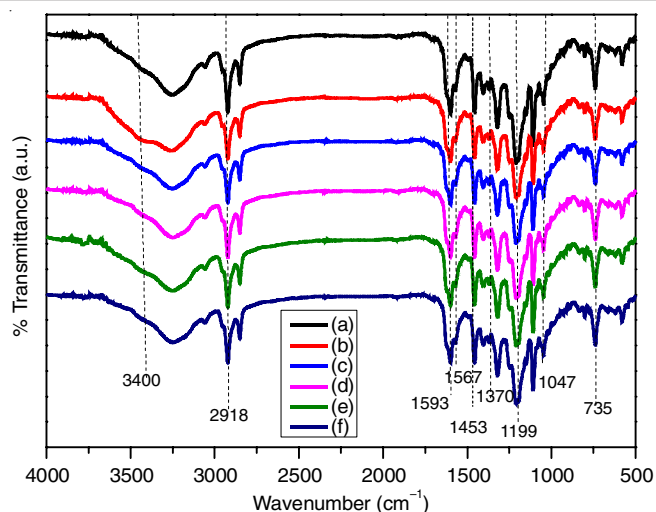


Fig. 2. FT-IR spectra of (a) PIn-5M (b) PIn-5D (c) PIn-20M (d) PIn-20D (e) PIn-40M and (f) PIn-40D

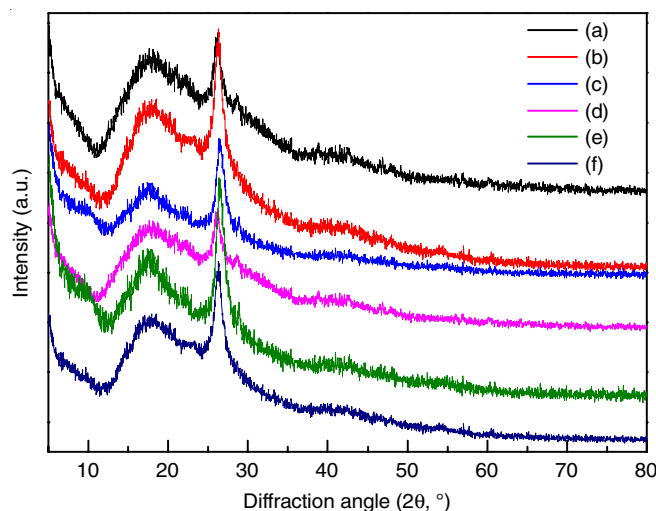


Fig. 3. XRD pattern of polyindole samples: (a) PIn-5M (b) PIn-5D (c) PIn-20M (d) PIn-20D (e) PIn-40M (f) PIn-40D

EDS analysis: The elemental analyses of synthesized polyindole samples were carried out by using XPS as shown in Fig. 4. The presence of C, O, N and S has been confirmed from XPS spectra as shown in Fig. 4a. The elemental shoulders of S and O are appearing due to remaining content of APS and moisture content. Moreover, the presence of C1s and N1s shoulders around 284.68 eV and 400.2 eV in the XPS spectrum of polyindole confirmed the polymerization of indole [21].

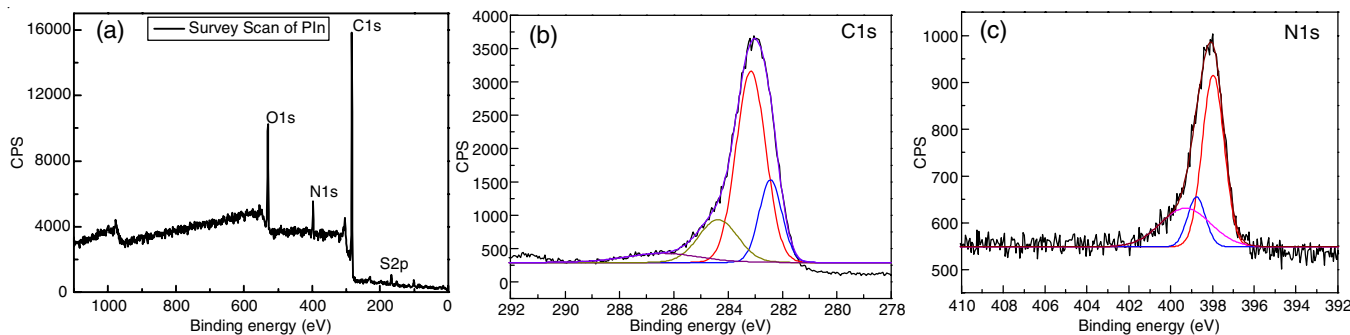


Fig. 4. XPS spectra of synthesized polyindole samples (a) Survey scan and high-resolution spectra of C1s (b) and N1s (c)

Thermal studies: The thermal stability of polyindole sample (PIn-20M) was investigated by using TGA under N₂ atmosphere as shown in Fig. 5. The decomposition of polyindole sample in the temperature range from 100-200 °C is due to the loss of trapped moisture content as well as the presence of oligoindole residues [47]. In addition, the surfactant SDS present in the sample start to degrade at the temperature range of 200-300 °C [48]. Moreover, as the temperature rises, the degradation of polyindole skeletal backbone started above 400 °C [49].

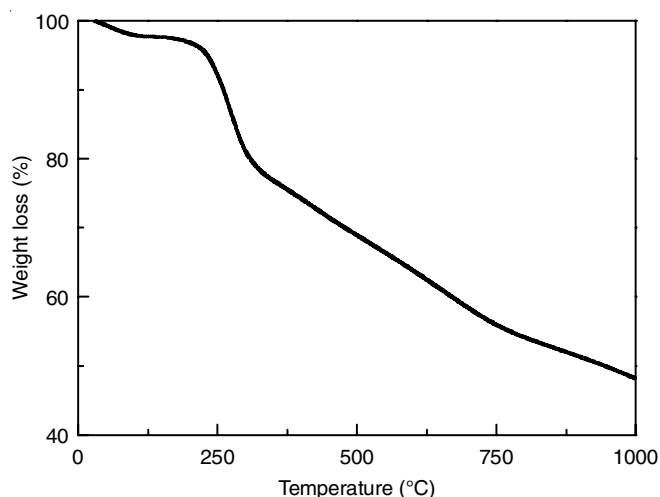


Fig. 5. TGA curve of synthesized PIn-20M under N₂ atmosphere

FESEM studies: FESEM images of different polyindole samples synthesized by using SLCs under mixed and diffused conditions at 5, 20 and 40 °C are shown in Fig. 6. The polyindole samples under diffused conditions at 5 and 20 °C (Fig. 6a and c) showed rod-like nanostructures, whereas, polyindole synthesized under the mixed conditions (Fig. 6b and d) but at similar temperature conditions showed spherical morphology. The difference in the morphology of polyindole may be attributed to the difference in the rate of polymerization during mixed and diffused conditions. The previous investigations explained well that under diffusion conditions the rate of polymerization is slow and under mixed conditions the rate of polymerization is fast [50]. Thus due to the difference in the rate of polymerization, the difference in polyindole nanostructures morphology is also observed.

It is also investigated that the SLCs confinement effect dominated only up to 20 °C. To further verify this observation, the SLCs assisted 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 in nature. The mesophase becomes unstable in both cases *i.e.* under mixed and diffusion conditions. Thus, the SLCs mesophase confinement effect on controlling the nanostructures morphology is absent under diffusion conditions as well.

The polarized optical microscope images for the confirmation of SLCs are shown in Fig. 7. The electrochemical activity of polyindole samples were also studied using cyclic

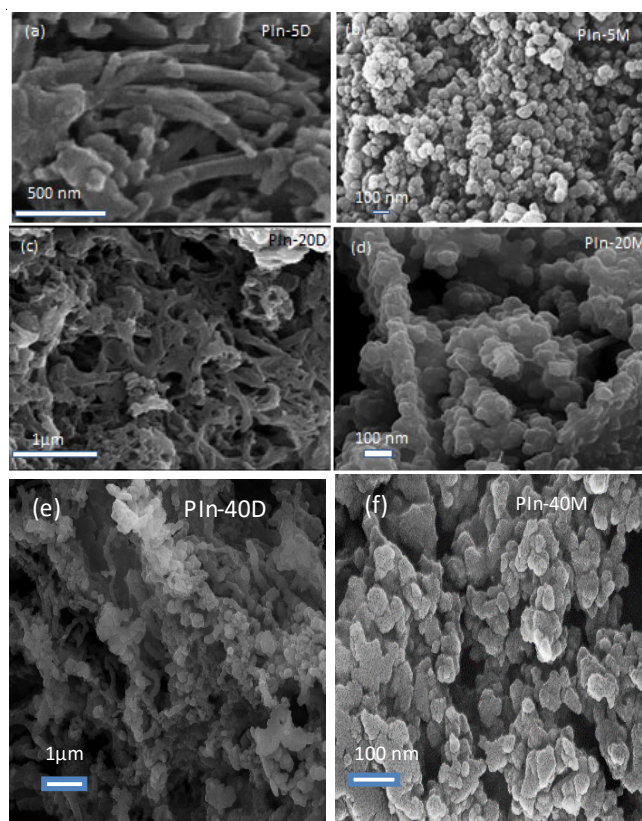


Fig. 6. FE-SEM images of different synthesized polyindole samples using SDS as surfactant in mixed as well as diffused condition (a) PIn-5D (b) PIn-5M (c) PIn-20D (d) PIn-20M (e) PIn-40D (f) PIn-40M

voltammetry (CV), which is recorded at different scan rates at 0.1N H₂SO₄ as electrolyte (Fig. 8).

Eqn. 1 is used for calculation of gravimetric specific electrochemical capacitance (C_{sp}) [51]:

$$C_{sp} = \int \frac{IdV}{vmV} \quad (1)$$

where, I represent the response current, V signifies the potential window (V), v indicates the potential scan rate (mV s⁻¹) and m stands for the mass of the active material in the electrode. The calculated specific capacitance (C_{sp}) of all polyindole samples is given in Table-1.

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

Conclusion

Using swollen liquid crystals (SLCs) as soft templates at different temperatures can easily control polyindole nanostructures morphology. In this work, spherical morphology of polyindole 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}).

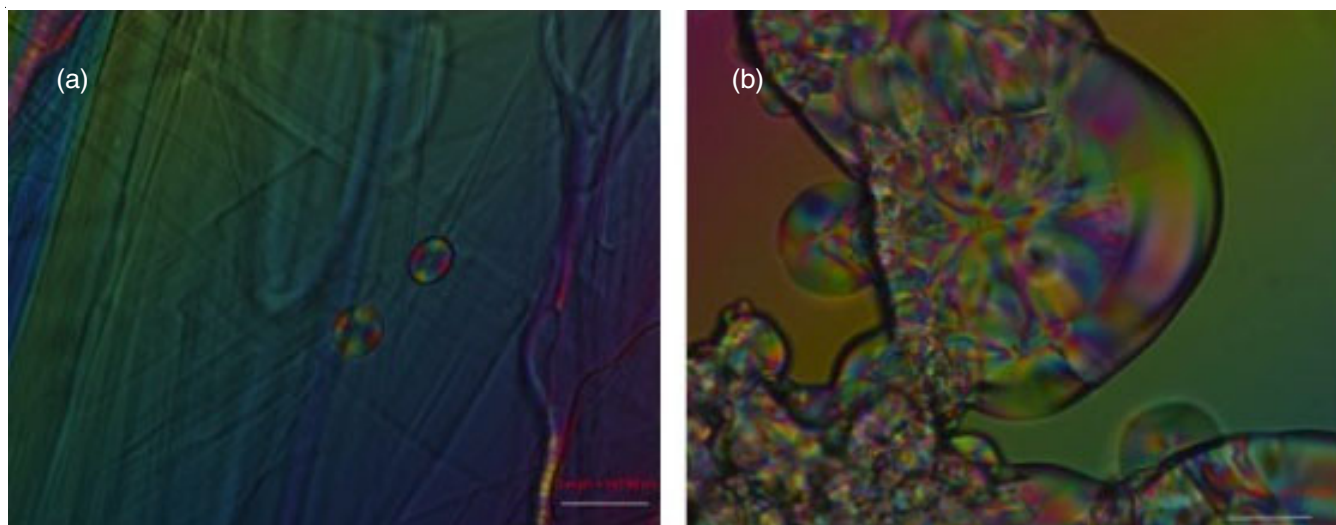


Fig. 7. Polarized optical microscope images (a) At the time of preparation of SLC (b) Confirmation of SLC

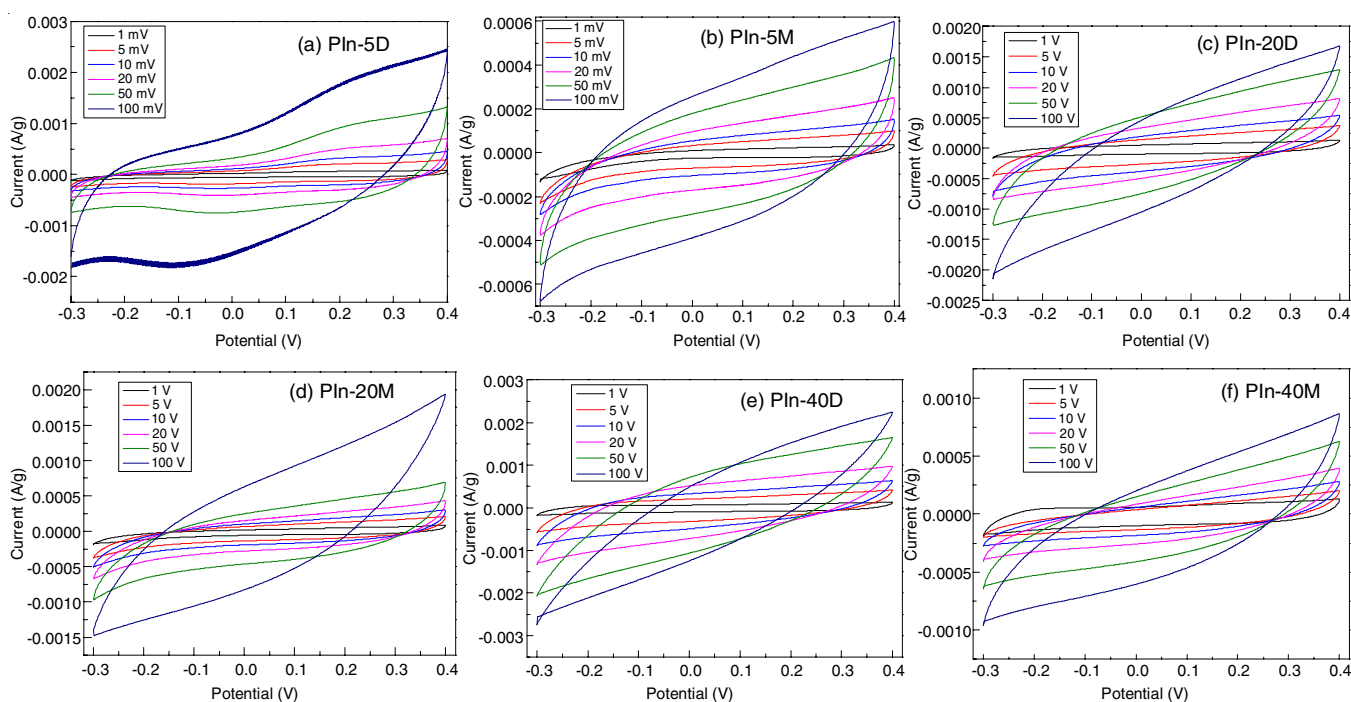


Fig. 8. Cyclic voltammogram of different polyindole samples in 0.1N H_2SO_4 : (a) PIn-5D (b) PIn-5M (c) PIn-20D (d) PIn-20M (e) PIn-40D (f) PIn-40M

TABLE-1
CALCULATED SPECIFIC CAPACITANCE (C_{sp}) OF ALL PIn SAMPLES

Scan rate (mV/s)	C_{sp} (F/g)					
	PIn-5D	PIn-5M	PIn-20D	PIn-20M	PIn-40D	PIn-40M
1	54.6075	77.5510	191.2314	90.5760	260.4100	228.4751
5	29.8273	33.8740	103.8118	41.4600	161.3290	54.8941
10	20.4200	23.8136	77.7205	29.5000	125.3642	37.9957
20	27.7200	18.4338	52.8597	21.0400	95.7600	26.9512
50	12.5274	11.8846	32.8623	13.3565	61.0660	17.3288
100	13.0290	8.2984	23.0000	14.5200	38.7290	12.6742

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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