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Effect of Synthesis Temperature on Properties of Polyaniline

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Abstract

The effect of synthesis temperature on percentage yield, thermal stability, surface morphology, crystallinity, and conductivity of polyaniline doped with dodecylbenzenesulfonic acid (PANI-DBSA) was studied. PANI-DBSA was synthesized at and the 5, 10,20, 25 and 30 0C and the percent yield of the product was determined. Furthermore, thermo gravimetric analysis (TGA), scanning electron microscopy (SEM), X-ray diffraction (XRD), UV-Visible spectrophotometry and cyclic voltammetry (CV) were utilized to inspect the variation in different physicochemical properties of the synthesized polymer with changing synthesis temperature

Keywords: Temperature, PANI-DBSA salt, Yield, Inverse emulsion polymerization, doping level, electroactivity

INTRODUCTION

Conducting polymers have received enormous interest over the last decade resulting to an explosion of publications. The research in this area has provided the fundamental understanding of the chemistry, physics and material science of these materials and has supported the industrial growth of conducting polymer products [1, 2]. Several kinds of intrinsically conducting polymers (ICPs) have been produced and are widely in use due to reasonably high conductivity, which include polypyrrole (PPy), polythiophene (PT), polyacetylene (PA), polyparaphenylene (PPP) and polyaniline (PANI) etc. [3].

Among these ICPs PANI is a common conductive polymer and one of the most representative of pseduocapacitive materials. Since it was first synthesized in 1886, PANI has become the most promising conductive polymer, due to its easy synthesis, low cost, good conductivity, special doping mechanism, excellent wave absorption, and electrochemical performance [4]. PANI is polymerized by oxidation of an aniline monomer [5]. Aniline is one of the most important amines and it is mainly used in the manufacture of dyes, drugs, resins, and as a rubber vulcanization accelerator. Therefore, PANI is the cheapest and the most thermally stable of intrinsically conductive polymers [6].

Varieties of methods are applied to synthesize PANI. However, two principal methods are frequently applied. 1) Electrochemical method of polymerization. 2) Chemical method of polymerization. Electrochemical polymerization is generally carried out in a cell of three electrode system i.e. a reference electrode, counter electrode, and working electrode. Chemical polymerization of PANI can be carried out using aniline monomer, a dopant (e.g. strong protonic acid) and an oxidant in an appropriate solvent [7]. Large scale production of PANI can be achieved by chemical polymerization [8]. Chemical polymerization includes various techniques i.e. solution, emulsion / inverse emulsion, interfacial, metathesis, seeding, sonochemical and self-assembled polymerization [9]. Emulsion and inverse emulsion polymerization techniques have been found to be superior to other polymerization techniques, because polymerization process can easily be controlled in these technique [8].

Emulsion polymerization involves dispersion of the monomers in aqueous phase forming a uniform emulsion. Varieties of surfactants are used to stabilize emulsion during polymerization reaction [9]. Therefore, it is a stabilized colloidal dispersion. The reaction is proceeding in a large number of loci, which are dispersed in the dispersion medium (continuous phase). Emulsion polymerization is considered the fruitful method for the synthesis of soluble PANI [10, 11, 12, 13, 14]. During emulsion polymerization, aniline monomer, protonic acid and a proper oxidant are combined with a mixture of polar solvent (usually water) and a non-polar / weakly polar solvent (e.g. chloroform, toluene, or xylene) which is insoluble or

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sparingly soluble in water. The formation of a stable emulsion requires an emulsifying agent such as DBSA. The product cannot be directly isolated from the reaction mixture because the prepared PANI salts remain entrained in emulsion to the end of reaction with simultaneous formation of byproducts. In majority of the cases, isolation of the product is accomplished by breaking of the emulsion i.e. separation of aqueous and organic layers, collection of PANI salt through a suitable solvent, followed by filtration and washing [15, 16].

On the other hand, inverse emulsion polymerization is totally opposite to conventional emulsion polymerization (i.e. oil in water emulsion). It is water in oil emulsion i.e. aqueous phase is dispersed in a weakly polar or non-polar organic dispersion medium. This type of polymerization consists of dispersion of an aqueous phase of monomers (dispersed phase) in a non-polar organic phase (dispersion medium). Initiation of polymerization is achieved through lypophilic initiators. The reaction proceeds through numerous loci dispersed in the dispersion medium [17]. Inverse emulsion polymerization also has a number of advantages. This technique suffers to a very less extent from thermal and viscosity problems as compared to the other techniques. The product can be directly utilized without any further separation in most of the cases. The rate of polymerization reaction is high during this process. It yields higher molecular weight polymers [18, 19].

Generally, it has been observed that increase in temperature is accompanied by increase in the polymerization rate of PANI-DBSA salt. Reduction in the propagation step of PANI-DBSA salt is observed with increase in temperature along with distinct intermediate stages. These intermediate stages correspond to different oxidation stages of PANI-DBSA salt, which decrease with increase in temperature [20]. Dielectric permittivity of PANI-DBSA and poly (vinylidene fluoride) (PVDF) composite has been found to increase by 60% by increasing the temperature from 25 ∘C to 115 ∘C [21]. Electrical conductivities also show variation with temperature. Electrical conductivity of PANI has inverse relation with temperature. Maximum conductivity is found at lower temperature. It is due the fact that polymer chains are more orderly arranged at lower temperature and have higher molecular mass [22]. Similarly, electro polymerization of aniline is also dependent on temperature. Anodic peak, which represents the formation of anilinium cation, shifts towards more negative values with increase in temperature. This indicates that increase in temperature favors the initiation step [23]. It is assumed that lower temperature results in the formation of relatively more homogenous structure of PANI film, corresponding to the sharp peak in cyclic voltammogram. Broadening of the peak is observed with increase in temperature, which indicates deformation of the polymer chain. The rate of polymerization increases by increasing the temperature from 0 ∘C to 20 ∘C and then decreases by further rise in temperature. The credit of this odd behavior is given to decrease in conductivity, poor electro activity, and disintegration of the polymer film at higher temperature [24].

This dissertation deals with the synthesis of PANI-DBSA salts at different temperatures using inverse emulsion polymerization technique. Water was used as dispersed phase and a mixture of 2-butanol and chloroform was employed as dispersion medium. The emulsion was stabilized by using DBSA as a surfactant. DBSA also act as an active dopant during the polymerization process. Oxidation of polymer was accomplished by benzoyl peroxide.

Experimental

Chemicals

Chemicals utilized are: Aniline (Acros) as a monomer, Benzoyl peroxide (BPO) (Scharlau) as an oxidant, Chloroform (Scharlau) and 2-butanol (Aldrich) used as dispersion medium, Dodecyl benzenesulfonic acid (DBSA) (Aldrich) as a dopant as well as a surfactant, Dimetyl sulfoxide (DMSO) (Acros) as a solvent for polymer, Tetrahydrofuran (THF) (Scharlau) used as a solvent for polymer, Acetone (Scharlau) used for washing of the precipitate. All the chemicals were of analytical grade.

METHODOLOGY

Synthesis of PANI-DBSA Salts

During experiment, the temperature was controlled by means of a double wall reactor and a thermostat. First of all, 0.29 moles (25mL) of chloroform was added to the double wall reactor followed by addition of 1.25×10^{-3} moles (0.303g) of benzoyl peroxide (BPO) with continuous stirring on a magnetic stirrer at constant stirring rate. 0.13 moles (10mL) of 2-butsnol, 3.73×10^{-3} moles (1.2mL) of DBSA and 5.36×10^{-4} moles (0.05mL) of aniline monomer were added to the above mixture. A milky emulsion was produced by addition of 0.28 moles (5mL) of Millipore water. The temperature of reaction mixture was kept constant at 25 ∘C. The polymerization reaction proceeds for 24 hours. The reaction mixture turned from a white milky solution to a dark green color in about 5 hours. After 24 hours, the reaction mixture was introduced into separating funnel and was allowed to stand for 1 hour. The two immiscible layers were separated out from each other i.e. non aqueous organic upper layer containing the dark green PANI-DBSA salt and lower aqueous layer. The lower aqueous layer was removed from the separating funnel in a beaker while the upper layer was collected in a petri dish. The organic layer was allowed to dry in petri dish at room temperature, which resulted in the formation of PANI-DBSA film. This film broke down into flakes when treated with small amount acetone. Then it was filtered and washed by 80mL of acetone to remove all of the oligomers from PANI-DBSA salt. It was followed by drying of the precipitate in a desiccator. After drying, the precipitate was weighed.

The same experimental process, mentioned above was performed at different temperatures i.e. 30, 35, 40, and 45 ∘C. The PANI-DBSA salts synthesized at these temperatures were labeled as, PANI 25, PANI 30, PANI 35, PANI 40 and PANI 45 respectively.

Precipitate of PANI-DBSA formed at 30 ∘C required about 100 mL of acetone for washing. During the polymerization at 35, 40, and 45 ∘C, the milky solution changes to dark green solution through intermediately brown color in 3-4 hours indicating higher rate of oligomerization. After 24 hours, the solutions were dark brown in color that repre-sented higher concentration of oligomers as compared to polymers. Due to this reason, a large quantity of acetone ranging from 130-150 mL was required for the washing of pre-cipitate at these temperatures.

Characterizations

Percentage yield of the polymer was determined with the help of the following expression [25]:

$$ \text{Percentage Yield} = \frac{\text{Mass of PANI-DBSA}}{\text{Mass of Aniline} \times \text{Mass of DBSA}} \times 100 $$

UV-Vis spectra of PANI-DBSA salts were obtained using Perkin Elmer Spectrophotometer (UK). Cyclic voltammogram was recorded using DY2323 Bipotntiostat (Japan). Scanning electron microscopy of PANI-DBSA salts was carried out through JSM910 (JEOL Japan) scanning electron microscope. XRD was performed by Cu Kα radiations (λ= 1.5405 A∘) using Rigaku X-ray diffractometer (Japan). Thermo gravimetric analysis (TGA) was conducted using Perkin Elmer (USA) in N_2 atmosphere at heating rate of 10 ∘C/min.

RESULTS AND DISCUSSION

Effect of Preparation Temperature on% Yield

Effect of preparation temperature on the% yield of PANI-DBSA salt is given in Table 1. Maximum% yield was observed at room temperature (i.e. 25 ∘C). Afterwards, the yield decreases with increase in temperature (Figure 1). At 30 ∘C a decrease of 7.37% was observed as compared to maximum yield obtained at 25 ∘C. Greater decrease of about 32.24% and 43.60% was observed in the yield at 35 ∘C and 40 ∘C respectively. Maximum decrease in the% yield was recorded at 45 ∘C.

Decrease in the% yield with increase in the temperature may attribute to increase in the polymerization rate and formation of polymers with lower average molecular mass. An increase in the temperature favors reduction of propagation step of the polymer chain, which results in the formation higher concentration of oligomers. Furthermore, at lower temperature the polymer chains are arranged in more regular manner which also assists higher average molecular mass of the polymer [20, 26]. A lower yield at 30 °C can be credited to formation of polymers with lower average molecular mass. Greater decrease at further higher temperatures is due to the higher concentration of oligomers and their subsequent loss during washing of the precipitate with acetone. This effect was more pronounced at 45 °C.
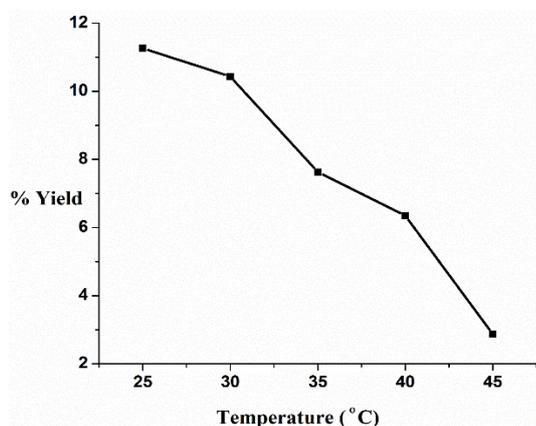
Figure 1: % Yield vs. temperature plot for PANI-DBSA salts

Table 1: Variation in the% yield with increase in temperature

S. No	Sample codes	Temperature (°C)	% Yield	% Decrease in Yield
1	PANI 25	25	11.26	.....
2	PANI 30	30	10.43	7.37
3	PANI 35	35	7.63	32.24
4	PANI 40	40	6.35	43.60
5	PANI 45	45	2.87	74.51

Effect of Reaction Temperature on Surface Morphology

Size and shape of the PANI-DBSA particles were analyzed through scanning electron microscopy (SEM) at 10,000 times magnification at a voltage of 15 kV. The magnification range of SEM is well suited for exploring micro, semi-micro and even nanostructure of PANI. SEM images can be helpful in the correlation of crystallinity, electrical conductivity, mechanical properties etc of the polymer with surface morphology. Figure 2 show the SEM images PANI-DBSA salts synthesized at different temperatures. These micrographs represent the typical agglomerated or granular morphology of PANI-DBSA salt [27, 28, 29].

The SEM images reveal that PANI-DBSA flakes have irregular geometry and have sharp edges. The difference in surface morphology of this PANI-DBSA salts lie in the size. The particle size shows a gradual decrease with increase in the synthesis temperature. The polymer synthesized at 25 °C has larger particle size in the range of 3-8 μm having relatively smooth surfaces. At 30 °C, the polymer presents a slight decrease in particle size ranging from 1.5-6 μm. The PANI-DBSA salt synthesized at a temperature of 35 °C also show the same morphology but with greater number of smaller particles. Further reduction in the size was observed at 40 and 45 °C ranging from 0.5-5 μm approximately which is in agreement with the literature [30]. The size of the PANI-DBSA flakes increases with simultaneous improvement in the regularity at lower temperature which can be credited to increase in the length of the polymer chain [31].
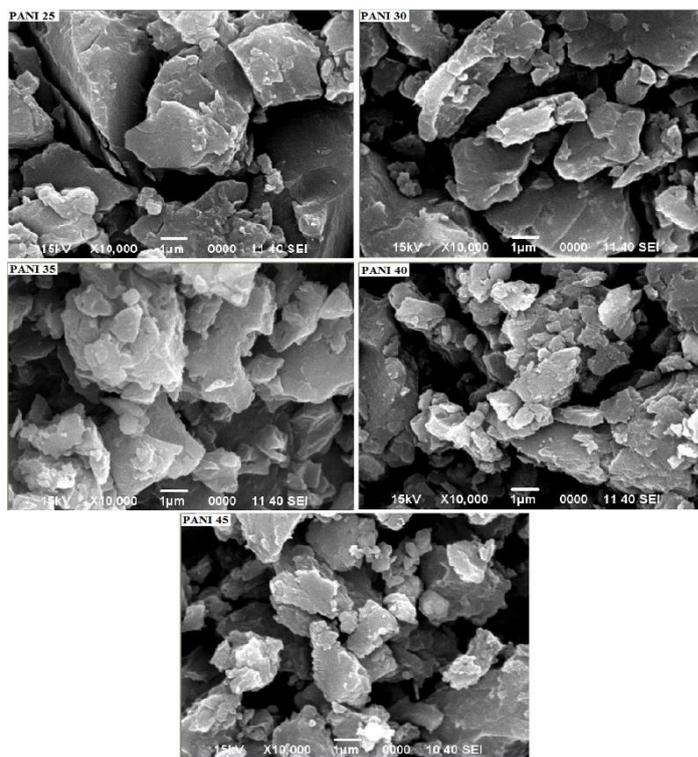
Figure 2: SEM images of PANI 25, PANI 30, PANI 35, PANI 40 and PANI 45

X-ray Diffraction Study of Doped Polyaniline

XRD has proven to be very effective in identifying the crystalline or amorphous nature of materials. It is a very simple and non-destructive technique. Figure 3 show the X-ray diffractograms of PANI-DBSA salts synthesized at different temperatures. These diffractograms reveal that all the PANI-DBSA salts show amorphous nature with a slight difference. Crystallinity increases to a very less extent with increase in the temperature. This can be assigned to less doping extent of DBSA in PANI chain because increase in doping extent of DBSA causes decrease in Crystallinity of PANI-DBSA salts [32].

All PANI-DBSA salts show the typical peaks at $2\Theta \approx 18°$, $20°$, $21°$, $23°$ and $25°$ with a number of additional peaks [33]. The peak at $2\Theta \approx 20°$ may be credited to periodicity parallel to the polymer chain [34], and the one at $25°$ may be attributed to periodicity perpendicular to the polymer chain [23, 33]. Other peaks may be ascribed to branches of DBSA doped in the polymer chains in various directions. The peaks at $2\Theta \approx 19°$ and $25°$ are related to the Vander Waals distances between the aliphatic chains and between the successive layers of phenylene rings [35, 36]. The comparison of 2Θ values having significant intensities along with corresponding d values for different PANI- DBSA salts is given in Table 2.
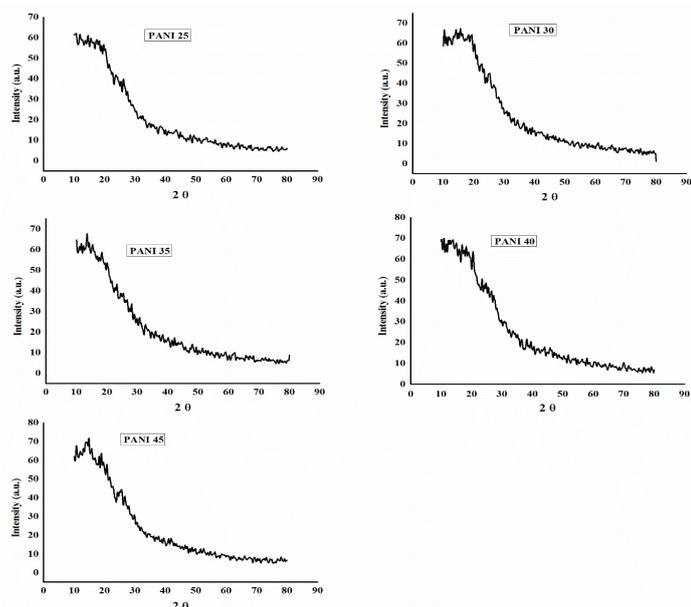
Figure 3: XRD spectra of PANI 25, PANI 30, PANI 35, PANI 40 and PANI 45
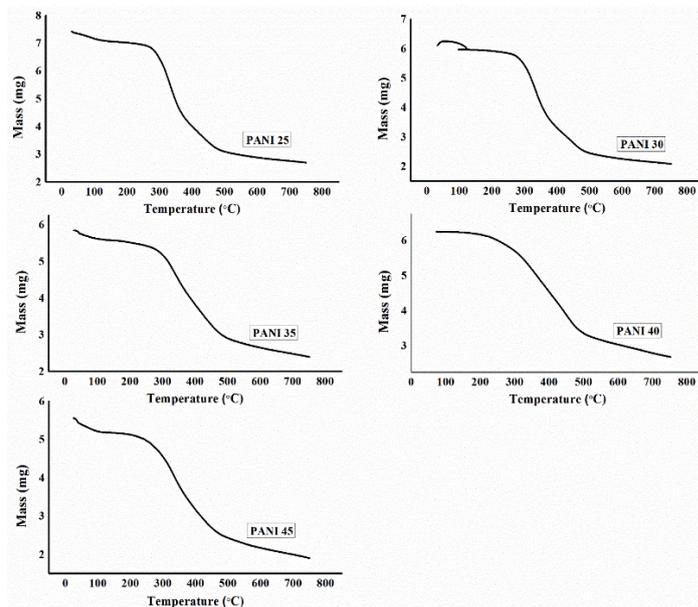
Figure 4: TGA curves of PANI 25, PANI 30, PANI 35, PANI 40 and PANI 45

Table 2. Comparison of 2Θ and d values of PANI-DBSA salts

S. No.	PANI 25		PANI 30		PANI 35		PANI 40		PANI 45	
	2Θ (degree)	d-value (A°)	2Θ (degree)	d-value (A°)	2Θ (degree)	d-value (A°)	2Θ (degree)	d-value (A°)	2Θ (degree)	d-value (A°)
1	14.6	6.042	10.4	8.507	11.7	7.570	10.9	8.132	10.8	8.177
2	16.5	5.375	14.4	6.167	12.2	7.237	18.3	4.849	13.1	6.758
3	17.6	5.021	15.7	5.651	13.4	6.622	20.5	4.335	14.4	6.154
4	18.9	4.696	16.4	5.414	13.7	6.477	23.5	3.778	15.0	5.921
5	19.7	4.505	18.5	4.795	15.1	5.862	25.6	3.473	18.2	4.865

Thermogravimetric Analysis

Thermal behavior of PANI-DBSA salts synthesized at different temperatures was investigated using TGA to find conditions for best processing. TGA provides useful in-formation for calculating the quantity of dopant in the polymer chain. It can also be used to check the decomposition kinetics of polymer.

All PANI-DBSA salts show approximately the same level of thermal stability. Figure 4 shows thermograms of these PANI-DBSA salts. All PANI-DBSA salts show the typical behavior of weight loss in three steps [37]. About 2.5-6.5% weight loss was observed during the first step. This weight loss can be attributed to the loss of water from PANI-DBSA salts

in the range of 30-140 ∘C approximately. PANI show significant weight loss due to loss of water content as it has exceedingly hygroscopic nature. Traces of water content still remain in the polymer backbone even after drying in vacuum [38].

The step indicating second weight loss ranging from 180-497 ∘C indicating weight loss of 43-57%. This can be credited to thermal decomposition of DBSA due to which the interaction between PANI and DBSA is damaged [39]. A slow and steady weight loss was observed at 500 ∘C during third step. This was due to oxidative degradation of PANI [40]. A comparison of three step weight loss is shown in Table 3 for PANI-DBSA salts.

Table 3: Three step weight loss of PANI-DBSA salts

S. No.	Sample codes	1st Step	2nd Step	3rd Step
		Temperature Range (^{0}C) (% Weight Loss)	Temperature Range (^{0}C) (% Weight Loss)	Temperature Range (^{0}C) (% Weight Loss)
1	PANI 25	30-140 (4.73)	185-488 (53.17)	500
2	PANI 30	30-120 (2.76)	181-492 (57.15)	500
3	PANI 35	30-125 (3.95)	182-497 (45.94)	500
4	PANI 40	30-125 (4.32)	186-492 (43.69)	500
5	PANI 45	30-112 (6.34)	187-490 (49.50)	500

UV-Vis Spectroscopic Study

UV-Vis spectroscopic study is very important for detection of various oxidation forms of PANI. It provides qualitative information regarding doping level, conjugation extent, and existence of radical cation in PANI.

UV-Vis spectroscopy of PANI-DBSA salts were carried out in dimethyl DMSO, which was used as a solvent. Figure 5 show absorbance vs. wavelength plots of PANI-DBSA salts. Their absorbance maxima are listed in Table 4.
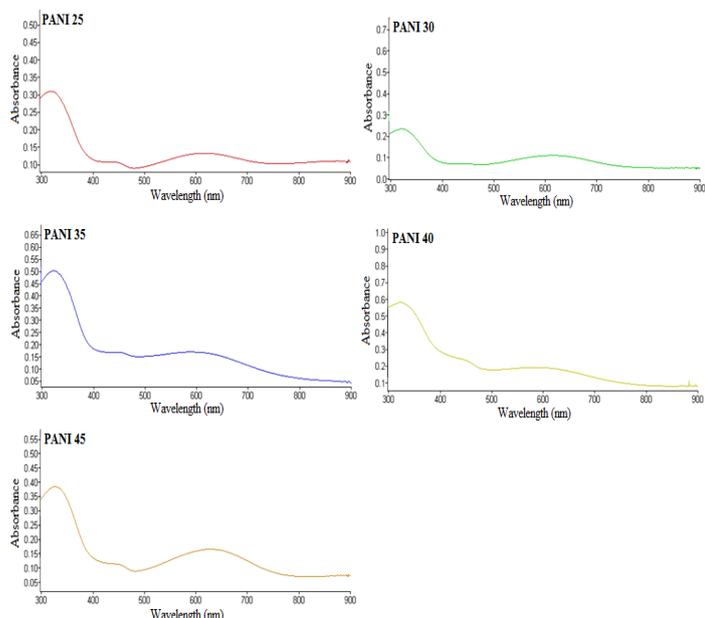
Figure 5: UV-Vis spectra of PANI 25, PANI 30, PANI 35, PANI 40 and PANI 45 in DMSO

Figure 6: Cyclic Voltammograms of PANI 25, PANI 30, PANI 35, PANI 40 and PANI 45 in DMSO

All PANI-DBSA salts show three maximum absorbance values having the range of 320-330nm, 433-440nm, and 584-628nm. Absorption peaks at 320-330nm arise from π-π* in phenyl rings corresponding to amine type of nitrogen in benzenoid segments of the polymer chain [41, 42, 43]. Absorption peaks at 433-440nm can be attributed to polaron transition [37, 44]. Peaks in the range of 584-628nm can be assigned to n-π* transition of exiton corresponding to excitation of imine nitrogen of quinoid segments of the polymer backbone [41, 42, 43].

The UV-Vis study of PANI-DBSA salts reveal that the absorption peaks shift towards lower wavelength region (i.e. blue shift) with rise in polymerization temperature. This is an indication of change in molecular configuration, which leads to the formation of shorter conjugate system. This increases the impact of required energy for the transition of π electrons due to higher energy gap [41].

Doping Extent

The doping extent of PANI-DBSA salts can be estimated through absorption spectra. The ratio of exiton transition to that of benzenoid transition gives an idea about the possible level of doping [37]. It is clear from Table 4 that the doping is more pronounced in the PANI 25 as compared to others. These results reveal that polymerization temperature plays an active role in doping of PANI.

Table 4: Absorption Maxima of PANI-DBSA salts

S. No.	Sample codes	Wavelength of Maximum Absorption (λ_{max}) (nm)			Doping Extent
		π-π*	Polaron	Bipolaron	
1	PANI 25	320	433	618	1.93
2	PANI 30	320	433	615	1.92
3	PANI 35	325	440	588	1.81
4	PANI 40	325	440	584	1.80
5	PANI 45	330	435	628	1.90

Cyclic Voltammetry

Electrochemical behavior of PANI-DBSA salts and interconversion of various oxidation states of these salts can be investigated through cyclic voltammetry (CV). It is not only a characterization tool for PANI-DBSA but also can be used for the synthesis of PANI-DBSA salts. It also provides useful information about the polymerization kinetics of PANI-DBSA salts. The peaks appearing in CV can be assigned to electrochemical behavior of PANI-DBSA salts. The relative positions of peaks provide clear information about the introduction of charges in the conversion of different oxidation states of PANI. Effect of different polymerization conditions i.e. anions, supporting electrolytes, polymerization medium and temperature can also be investigated through CV.

Representative CVs of five different PANI-DBSA salts synthesized at different temperatures are shown in Figure 6 using Ag/AgCl as a reference electrode at constant scan rate of 50 mV/s. A gold plate electrode was used as working electrode. All these salts show two oxidation (anodic) and two reduction (cathodic) peaks. The first anodic peak (Ea1) represents oxidation of leucoemeraldine form into emeraldine form while second anodic peak (Ea2) represents the conversion of emeraldine into fully oxidized pernigraniline form. In reverse, the first and second cathodic peaks (Ec1 and Ec2 respectively) show the transformation into emeraldine and then to leucoemeraldine form respectively [45]. Anodic and cathodic peaks of these salts appeared at different half potentials (EAg/AgCl) as a function of variation in polymerization temperature. First anodic peaks shift towards positive EAg/AgCl with increase in polymerization temperature. This can be ascribed to increase in the difficulty of conversion of leucoemeraldine into emeraldine form. Second anodic peaks shift towards negative EAg/AgCl with rise in temperature. This suggests the ease with which emeraldine form can transform into pernigraniline form [46]. Table 5 summarizes variation in electroactivity of PANI-DBSA salts.

Table 5: Electroactivity of PANI-DBSA salts

S. No.	Sample codes	E_{a1} (V)	E_{a2} (V)	E_{c1} (V)	E_{c2} (V)
1	PANI 25	0.0448	0.610	0.754	0.216
2	PANI 30	0.0725	0.590	0.730	0.236
3	PANI 35	0.130	0.545	0.652	0.264
4	PANI 40	0.144	0.518	0.648	0.236
5	PANI 45	0.151	0.569	0.620	0.227

CONCLUSION

PANI-DBSA salts were synthesized via inverse emulsion polymerization at five different temperatures i.e. 25, 30, 35, 40 and 45 °C. The percent yield was investigated at different polymerization temperatures. Percent yield was found to decrease with increase in temperature. Maximum yield was achieved at 25 °C. Surface morphology of PANI-DBSA salts was scrutinized through scanning elec-tron microscopy. The SEM images revealed the typical agglomerated morphology of PANI-DBSA salts. The size of PANI-DBSA granules was found to be dependent on polymerization temperature. The size of granules gradually reduced with rise in the syn-thesis temperature. X-ray diffraction analysis presented poor crystallinity of PANI-DBSA salts. The crystalline nature of PANI-DBSA salts has increased to a less extent with increase in polymerization temperature. Thermal stabilities were checked by thermogravimetric analysis. All the PANI-DBSA salts showed better thermal stabilities. They showed almost the same range of de-composition temperature for the polymer backbone. UV-Visible spectroscopy was utilized for the confirmation of DBSA incorpora-tion in the PANI chain. It also gave the idea about the doping extent of DBSA in the pol-ymer. The doping extent gradually decreased as the synthesis temperature for PANI-DBSA salts was raised. Electroactivity of PANI-DBSA salts were studied through cyclic voltammetry. Electroactivity was found to be dependent on the polymerization temperature. Electroactivity slowly decreased with increase in reaction temperature.

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