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Optically active poly[2-(*sec*-butyl)aniline] nanofibers prepared via enantioselective polymerization

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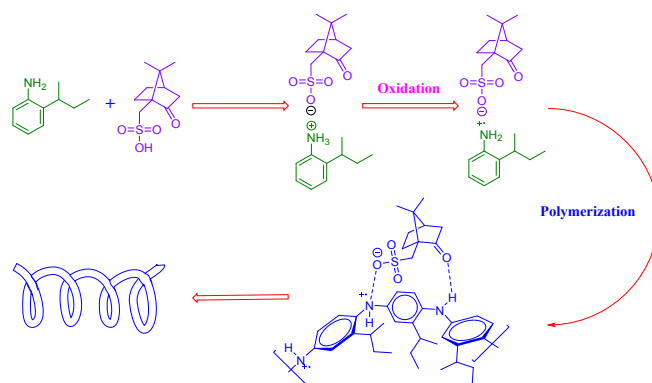
Abstract

In this paper we present a new synthetic route to optically active nanofibers of poly[2-(*sec*-butyl) aniline] (PSBA). Optically active PSBA nanofibers were produced by *in situ* chemical oxidative polymerization of a racemic monomer, (±)-2-*sec*-buthylaniline, in the presence of 1.5 M (+)- or (-)-camphor sulfonic acid (HCSA) with a monomer concentration of 0.025 M at 0 ºC. The mirror imaged circular dichroism spectra of both PSBA/(+)HCSA and PSBA/(-)HCSA show that the two polymers are optically active enantiomers and in this condition the chemical oxidation of 2SBA is an enantioselective polymerization. The produced polymer has uniform nanofibrillar morphology with average diameters of 55 nm according to scanning electron microscopy, and a number average molecular weight of 4680 g/mol as determined by gel permeation chromatography.

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Introduction

Chirality in polymers arises from helical conformations of polymer chains. A helical chain has two forms: one right-handed and the other left-handed, which together are known as enantiomers. If one of two helix forms is more prevalent, then the polymer becomes optically active.[1]

Conductive polymers have attracted a great deal of attention from many researchers because of their wide range of applications.[2,3] Among conductive polymers, polyaniline (PANI) is attractive because of its low cost, easy production, high environmental stability and potential for use in many applications such as sensors, printable electronics, actuators, supercapacitors, electromagnetic shielding, corrosion protection, biocomposites, filtration membranes and electro-optical applications among many others.[4-12]

In recent decades, chiral PANI has been extensively investigated and suggested for use in applications such as chiral recognition and enantiomeric separations.[13-14] Chirality in conductive polymers can be obtained either by polymerizing a chiral monomer, or by doping an achiral polymer with a chiral acid.[15-16] The first report for optically active PANI was presented by Wallace and coworkers wherein the optically active polymer was prepared through the enantioselective electropolymerization of aniline in the presence of either (+)- or (-)-camphor sulfonic acid (HCSA).[16] This same group then demonstrated that doping the emeraldine base form of polyaniline with a chiral acid in an organic solvent can also produce an optically active polymer.[17-20] Next, they prepared optically active PANI by *in situ* chemical oxidative polymerization of aniline and its derivatives in the presence of chiral acids in aqueous solution.[21-24] Kuramoto and coworkers synthesized optically active PANI and its derivatives in organic solvents via oxidative polymerization using 2,3-dichloro-5,6-dicyanobenzenquinone (DDQ) in the presence of either (+)- or (-)-HCSA.[25-27] Goto prepared a new optically active PANI derivative via polymerization of an optically active monomer.[15] The effect of copolymerization of aniline with substituted aniline on the conformation and optical activity of the generated nanofibers was further investigated.[28-30] The presence of substituted aniline in the polymer backbone causes a change in optical activity and in some cases a reversal of the helical form of the

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nanofibers. Therefore, the helical form and chiroptical properties of this polymer can be controlled to some extent.[28-30]

Since solubility of PANI in most organic solvents is low, its applications are limited.[31] Therefore, PANI derivatives (*ortho*, *meta* and *N*-substituted) have often been studied for practical purposes due to their higher solubility compared to the parent polymer.[22,31] One of these PANI derivatives is poly[2-(*sec*-butyl) aniline] (PSBA) which has good solubility in organic solvents and was first synthesized and characterized in our laboratory.[32-34] PSBA intrinsically is a chiral polymer because its monomer is chiral ((±)-2-*sec*-buthylaniline). Therefore, there are two ways to prepare optically active PSBA: (**1**) polymerization of the racemic monomer in the presence of a chiral dopant (as reported here), and (**2**) the resolution of the monomer into two enantiomers followed by polymerization of each enantiomer separately (currently under study).

For the generation of an optically active polymer, a single-handed helical conformation is needed.[1,19] In conjugated polymers placing a chiral anion dopant closer to the polymer backbone can facilitate the formation of a single screw helical conformation.[17,35]

For substituted PANI, a chiral dopant cannot approach the polymer chain as easily as it can the parent PANI, so that the formation of a one-screw helical conformation becomes more difficult when increasing the bulkiness of substituents from a hydrogen atom to a bulky substituent such as 2-*sec*-butyl.[17-18]

As shown in Scheme 1, as the bulkiness of the substituent (R) becomes larger, the ring-torsion angle of adjacent phenyl rings increases due to increased steric hindrance. This has a determinative effect on the preparation of a one-screw helical chain and also causes reduction in the basic strength of the polymer.[22,31]
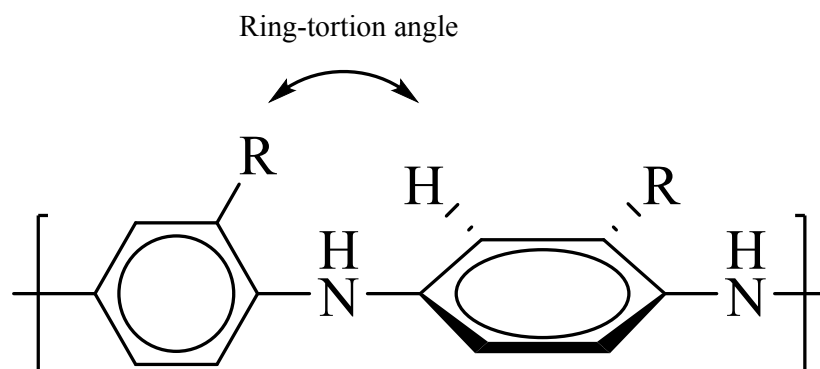
Ring-tortion angle

Scheme 1. Ring-torsion angle in PANI derivatives due to steric hindrance of the R substituent.

Kaner and Epstein with their co-workers separately have demonstrated the general template-free synthetic methods for making nanofibers of PANI and its derivatives by either interfacial polymerization or by rapidly mixing aniline, acid and oxidant as well as a dilute polymerization method.[36-45] They reported the formation of substituted PANI nanofibers such as polychloroaniline, polymethylaniline and polyethylaniline.[44-45] Until now, no published studies have reported on the formation of nanofibers from substituted PANI with bulky substituents such as propyl or butyl. In addition, attempts to prepare PSBA nanofibers via either interfacial polymerization or rapid mixing of aniline, acid and oxidant, have not been successful. In this study, we report the first successful synthesis of a nanofibrillar structure of PSBA as a bulky substituted PANI, by using a new method under special conditions. Since 2-sec-butyl is a bulky substituent, it causes the reactivity of the monomer to decrease which in turn complicates the creation of the nanofibrillar structure. Scheme 2 indicates the polymerization of 2SBA in the presence of camphor sulfonic acid and the different structures of PSBA.
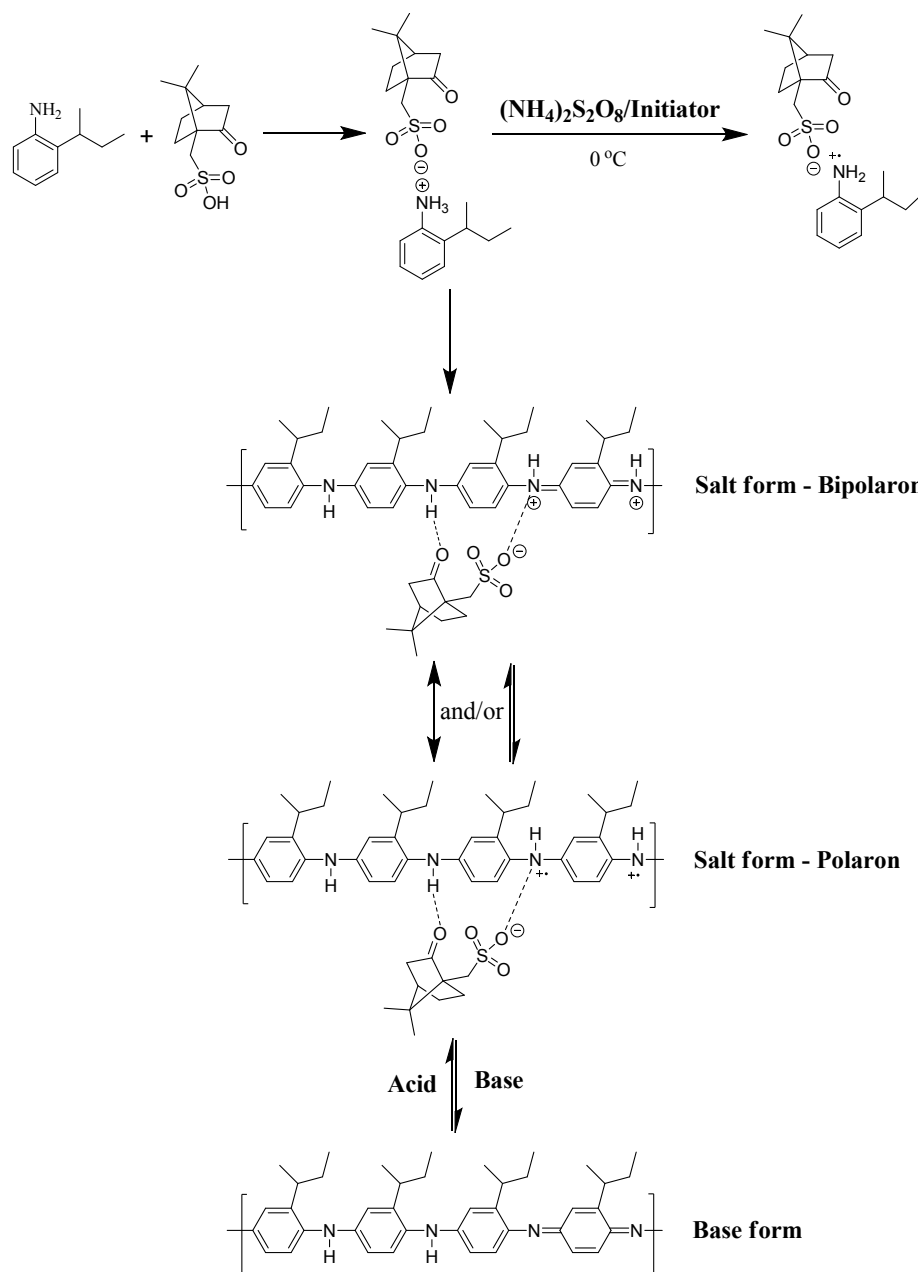
Scheme 2. Polymerization of 2-*sec*-butyl aniline in the presence of camphor sulfonic acid and the formation of the polaron, the bipolaron and the base form of PSBA**.**

Results and discussion

The generation of nanofibers through oxidation in aqueous acidic solution is an intrinsic property of PANI.[46-47] However, despite the parent PANI readily forming nanofibers, this is not the case with PANI derivatives under the same polymerization conditions and in most cases result in spherical structures.[44] This has been attributed to the lower rate of the polymerization reaction in substituted aniline relative to the parent aniline because of steric hindrance and electronic effects of substituents

on the ring or on the nitrogen atom. It has been suggested that the low rate of the polymerization

reaction leads to heterogeneous nucleation causing the nuclei to grow in all directions and form

agglomerated structures.[44,48-49] Therefore, in order to synthesize nanofibers of PANI derivatives,

homogeneous nucleation must be induced. For this purpose, the introduction of initiators such as

NPPD (aniline dimer) or 1,4-benzendiamine is needed. Initiators increase the rate of the reaction

leading to homogeneous nucleation that can produce nanofibrillar structures.[41-49]

In the present study, 2.5 mol% of NPPD was added as an initiator and the polymerization reaction of

2-SBA was carried out by two different procedures in aqueous solutions of either (+)- or (-)-HCSA at

a constant temperature of 0 °C via chemical oxidation with APS under various conditions such as

different molar ratios of oxidant to monomer and different acid concentrations. In all polymerization

reactions, the monomer concentration was 0.025 M.

In Method **1**, according to previous reports,[36-38] SEM images indicated that when the reaction vessel

was agitated for 15 seconds, nanofibers did not form, instead various structures including micro-

spheres and/or amorphous structures were created due to agglomeration of the PSBA nuclei (Figure 1,
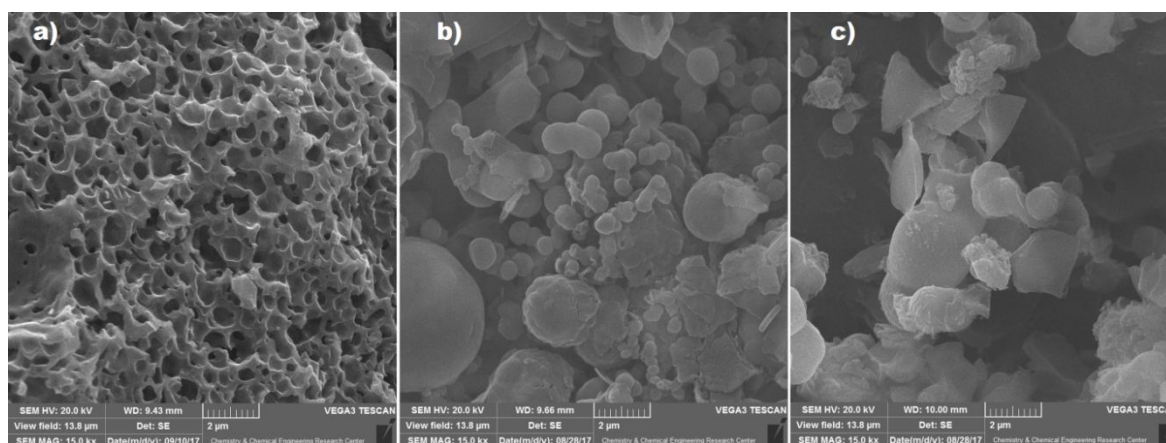
Polymers a, b and c).

Figure 1. SEM images of polymers formed using Method **1** which was agitated for 15 seconds at 0 °C under conditions of a) [HCSA]/[2SBA] = 40 and [APS]/[2SBA] = 1, b) [HCSA]/[2SBA] = 40 and [APS]/[2SBA] = 0.25 and c) [HCSA]/[2SBA] = 2 and [APS]/[2SBA] = 0.25.

In contrast, employing Method **2** resulted in nanofibers with an average diameter of 55 nm (Figure 2,

Polymers C and D). In order to study the effects of the HCSA to monomer molar ratio on morphology

and optical activity of the polymer, the polymerization reaction of 2-SBA was carried out by Method

2 under different acid concentrations including 0.025, 0.05, 1, 1.5, 2 and 3 molar. In other words, an

[HCSA]/[2-SBA] ratio of 1, 2, 40, 60, 80 and 120, respectively. With HCSA concentrations of 2 and 3

M, no precipitated polymer was observed; after 24 hrs the solution simply turned dark violet due to

the presence of short oligomers. This can be related to the high viscosity of the solution with an acid

concentration of 2M or higher. Under these conditions, the lower diffusion of reagents and monomer

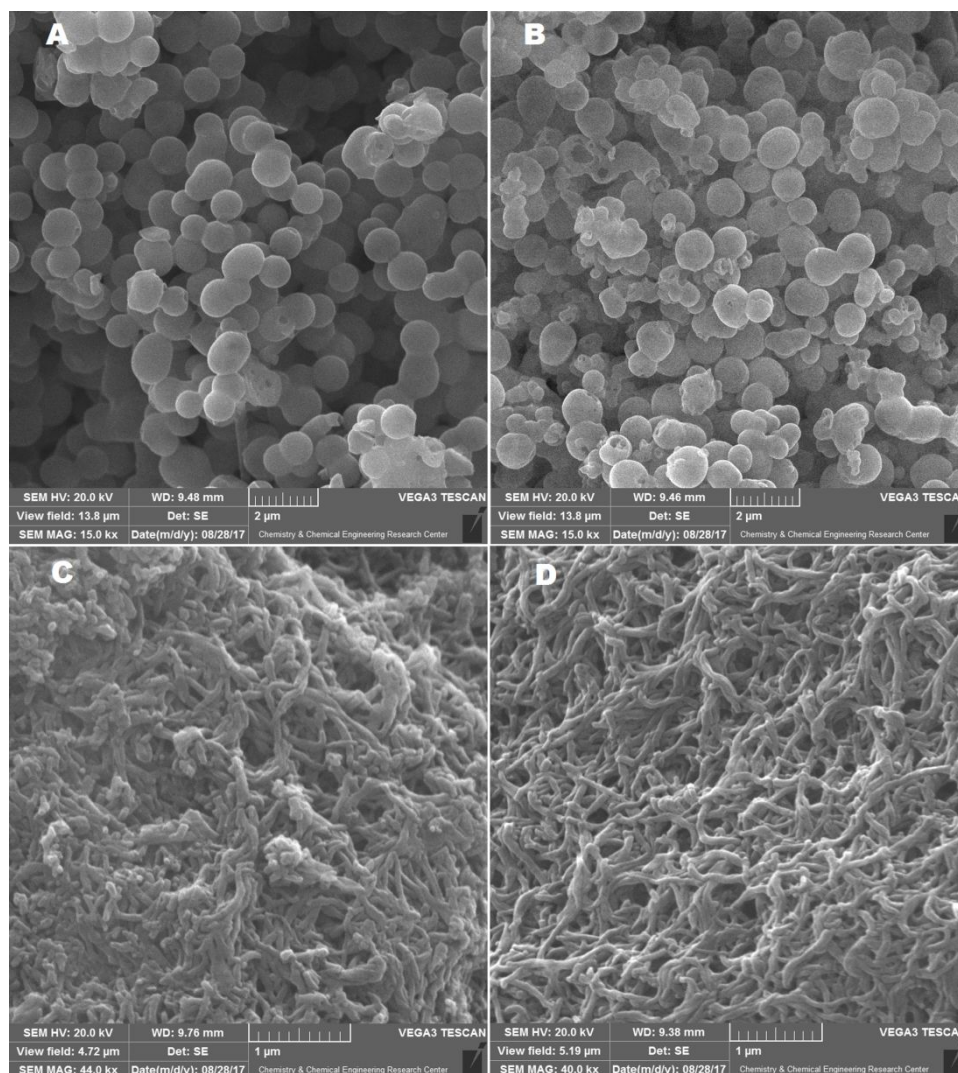prohibits the growth of polymer chains[29].

Figure 2. SEM images of polymers formed in Method **2** at a temperature of 0 °C and [APS]/[2SBA] = 0.25 with different

ratios of [HCSA]/[2SBA], A = 1, B = 2, C = 40 and D = 60.

Figure 2 shows SEM images, in the cases of A to D, the polymers were obtained in different molar ratios of [HCSA]/[2SBA] as 1, 2, 40 and 60, respectively. At a low ratio of HCSA to monomer (lower than 5), HCSA acts as an emulsifier, which causes the formation of micelles that fill with monomer. The micelles act as soft-templates, so oxidation leads to the formation of micro-tubes and/or micro-spheres[29] (Figure 2, A and B polymers). However, in higher ratios of [HCSA]/[2SBA], such as 40 or 60, HCSA plays the role of a protective agent and prevents heterogeneous nucleation which leads to the formation of nanofibrillar structures (Figure 2, C and D polymers).[29]

Figure 3 shows images of reaction vessels at the end of polymerization. As can be seen at a 2 M concentration of HCSA no precipitated polymer was observed; however, at 1 and 2 M acid concentrations nanofibers were produced which disperced in solution, whereas at 0.025 and 0.05 M acid concentration the produced polymer precipitated to the bottom of the vessel.
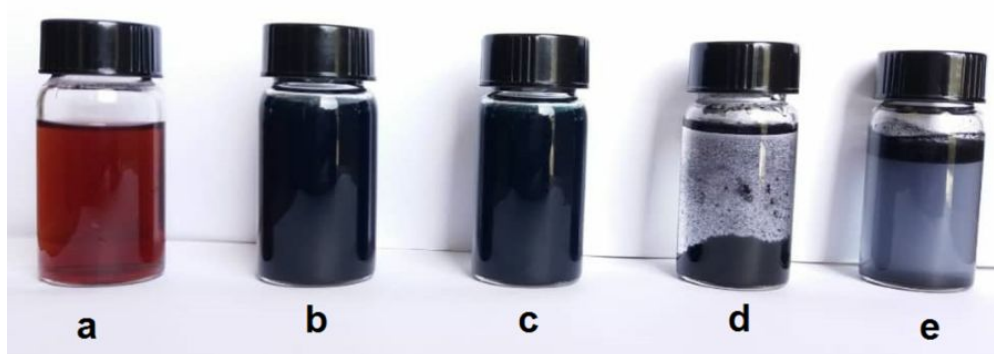

Figure 3. Images of reaction vessels after 24 hr under different HCSA concentrations: (a) 2 M, (b) 1.5 M, (c) 1 M, (d) 0.05 M and (e) 0.025 M.

Optically activity and morphology of the polymers formed by Methods **1** and **2** under different conditions are summarized in Table 1.

Table 1. Comparison of Polymers Formed Under Different Conditions

Entry	Specimen	Method of preparation	HCSA concentration (M)	[HCSA]/[2SBA]	[APS]/[2SBA]	Optically activity	Morphology
1	Polymer (a)	1	1	40	1	No	Porous
2	Polymer (b)	1	1	40	0.25	No	Microsphere
3	Polymer (c)	1	0.05	2	0.25	No	amorphous
4	Polymer (A)	2	0.025	1	0.25	No	Microsphere
5	Polymer (B)	2	0.05	2	0.25	No	Microsphere

6	Polymer (C)	2	1	40	0.25	No	Nanofibers
7	Polymer (D)	2	1.5	60	0.25	Yes	Nanofibers
8	-	2	2	80	0.25	No	No precipitated
9	-	2	3	120	0.25	No	No precipitated

The CD spectra of these polymers dispersed in deionized water are shown in Figure 4. As can be seen only one polymer is optically active – the one prepared in 1.5 M HCSA solution (Entry 7 in Table 1). Although in 1 M HCSA solution the nanofibrillar structure was obtained, these nanofibers do not exhibit optical activity (Figure 4, Entry 6 in Table 1).

In all CD spectra, the absolute magnitude of the CD bands could be estimated approximately from the mass of the polymer dispersed in water or dissolved in the organic solvent.
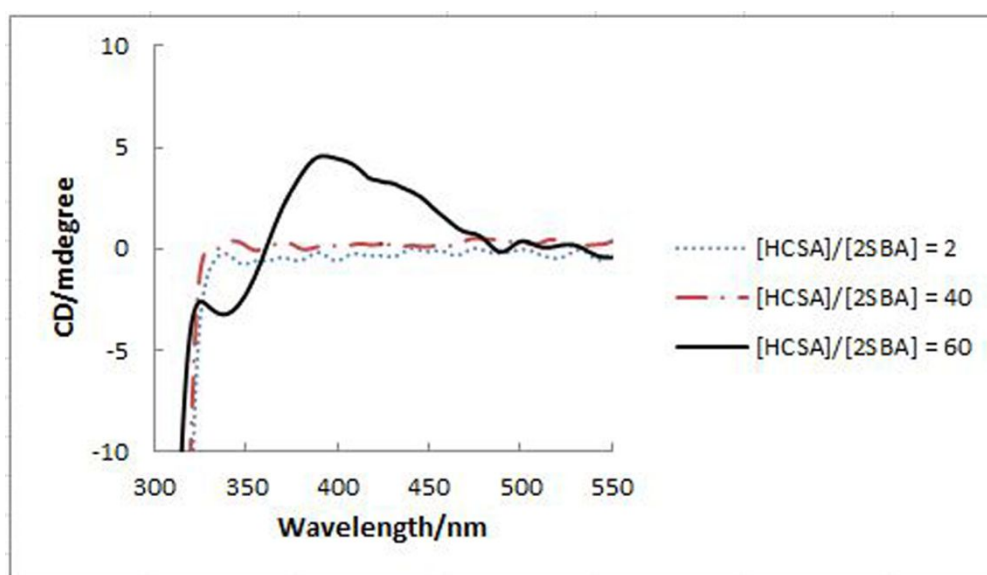

Figure 4. CD spectra of PSBA/(-)HCSA dispersed in water generated by Method **2** with [APS]/[2SBA] = 0.25 in different dopant acid concentrations.

Figure 5 shows the CD spectra of the nanofibers (Entry 7 in Table 1) dispersed in deionized water that were generated by Method **2** in 1.5 M aqueous solutions of both (+)- and (-)-HCSA. The mirror imaged CD spectra for both PSBA/(+)-HCSA and PSBA/(-)-HCSA indicate that the two polymers are optically active enantiomers. Each CD spectrum possesses five absorption bands at 200, 291, 335, 380

and 440 nm. The Cotton effect at 200 and 291 nm is related to the presence of the CSA anion in the polymer, whereas the bands at 335, 380 and 440 nm are associated with the optical activity in the polymer backbone. In addition, the peaks at 335 and 380 nm can be attributed to the bisignate exciton-coupled bands which are related to the benzenoid π-π* absorption band that one pair of this band partly overlaps with the CD band of the CSA anion. Moreover, the peak at 440 nm that partly overlaps corresponds to the low wavelength polaron absorption band.[26,29,50] This indicates that the chemical oxidation of 2-SBA is an enantioselective polymerization in the presence of either (+)- or (-)-HCSA with an acid concentration of 1.5 M and a molar ratio of [HCSA]/[monomer] of about 60.[16,29-30] At lower acid concentrations there does not appear to be sufficient acid dopants to produce a chiral polymer as has been observed in previous studies. [29-30]

The polymer chains formed under these conditions have a helical conformation. As mentioned above, the helical chain conformation has two forms: a right-handed form and a left-handed form, for which one of the two forms has been produced in a greater concentration than the other leading to the observed optically activity. When 2-(sec-butyl)aniline is dissolved in an HCSA aqueous solution under the proper conditions given above, the salt of anilinium camphor sulfonate is produced, in which the aniline molecules are surrounded by acid molecules. When the aniline is polymerized to produce the polymer chains, enantiopure HCSA causes the polymer chains to rotate primarily in one direction, forming a helical structure that leads to a chiral, optically active polymer.[18-19] This helical structure is preserved by electrostatic bonds of the sulfonate oxygen to polymer –**HN**$^{\cdot+}$– centers and hydrogen bonding of the CSA carbonyl groups to the –**NH**– sites of the polymer backbone (Scheme 2).[18-19]
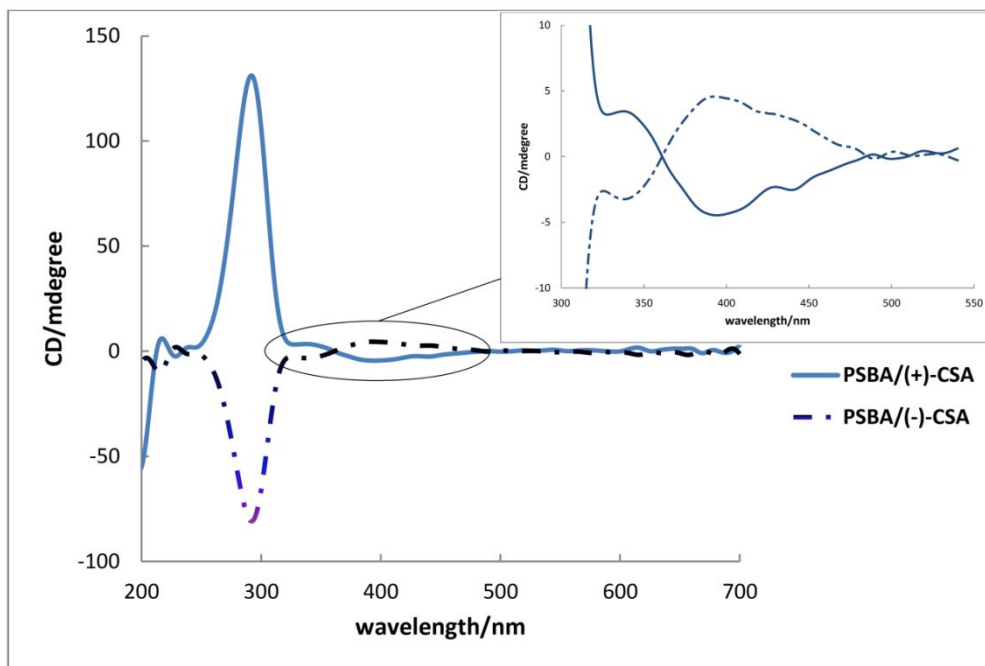
Figure 5. CD spectra of both PSBA/(+)HCSA and PSBA/(-)HCSA dispersed in deionized water generated in 1.5 M HCSA

aqueous solution with a 0.25 molar ratio of oxidant to monomer produced using Method **2** (Entry 7 in Table 1).

In order to obtain pure optically active polymer, the optically active salt form was de-doped with

NH_4OH 1 M aqueous solution both for PSBA/(-)HCSA and PSBA/(+) HCSA. Figure 6 presents the

CD spectra of the nanofibers dispersed in deionized water after de-doping. The mirror imaged CD

spectra for the two polymers (PSBA/(-)HCSA and PSBA/(+) HCSA) after de-doping, indicate that the

two polymers are optically active enantiomers. For comparison, CD spectra of the base form together

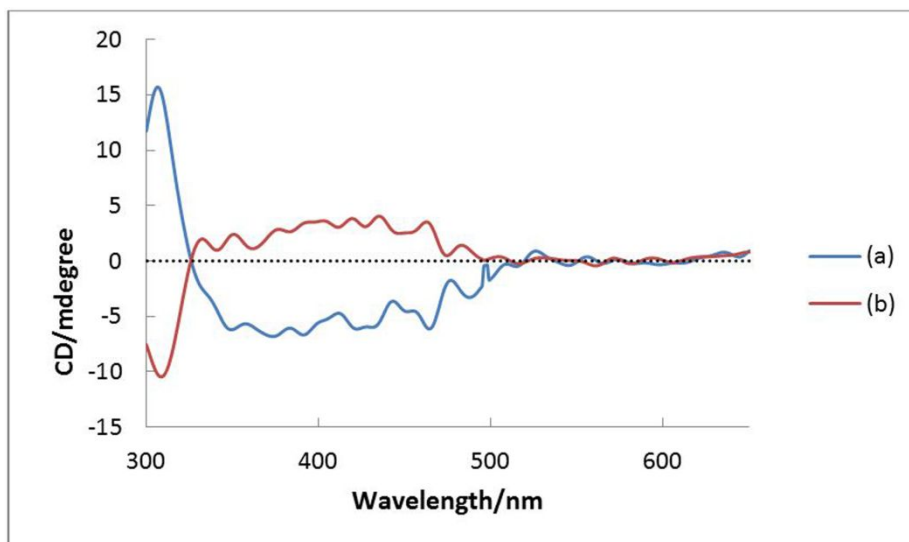with the salt form are shown in Figure 7.

Figure 6. CD spectra of optically active polymer dispersed in deionized water in the base form after de-doping with 1 M aqueous NH$_4$OH of both (a) PSBA/(+)HCSA and (b) PSBA/(-)HCSA.
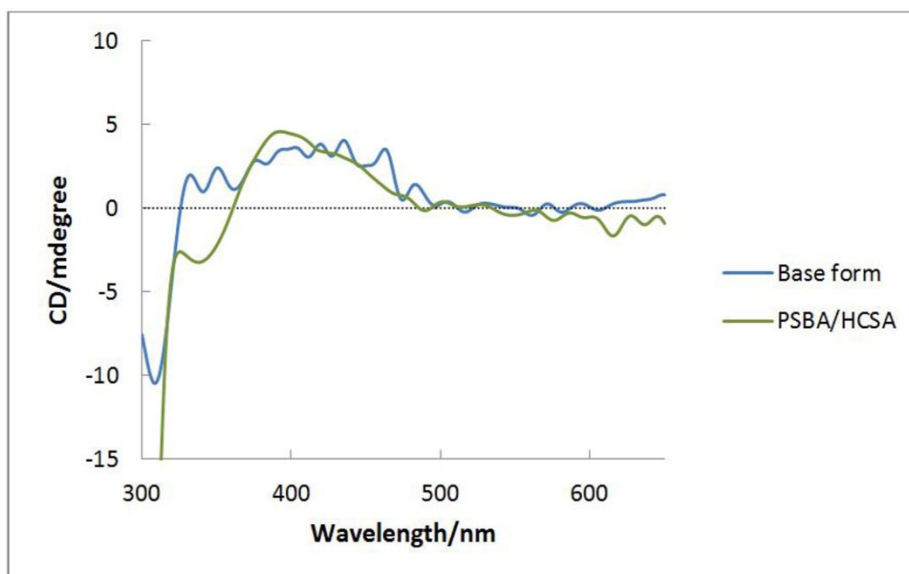

Figure 7. CD spectra of optically active polymer in both the base form and the salt form (PSBA/(-)HCSA).

In addition, we obtained optically active polymer in the salt form with an achiral acid after de-doping the optically active PSBA/HCSA with a NH$_4$OH solution and re-doping with a 1 M HCl aqueous solution. CD spectrum of this polymer is shown in Figure 8 indicating that the polymer is optically active with an achiral anion (Cl$^-$).
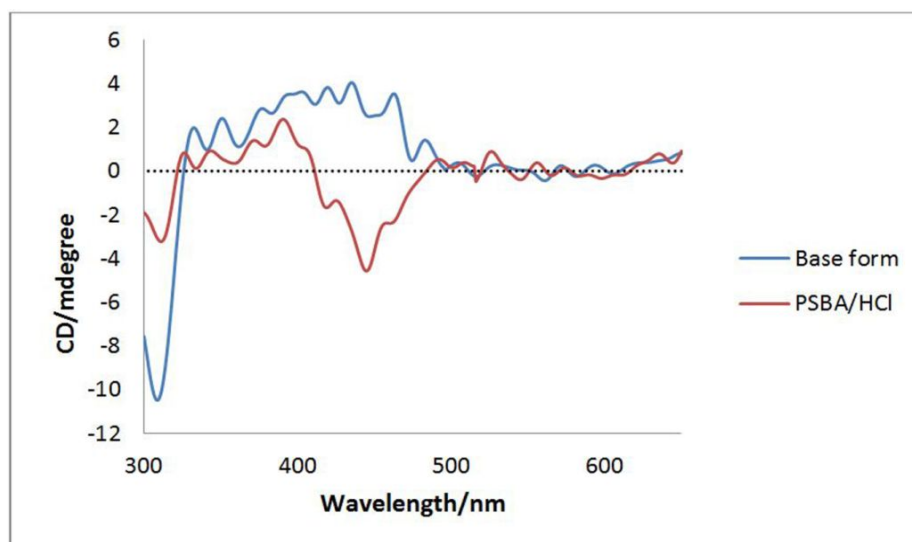
Figure 8. CD spectra of optically active polymer dispersed in deionized water after de-doping by NH$_4$OH 1 M aqueous solution (base form) and after re-doping by HCl 1 M aqueous solution (PSBA/HCl).

To study the chiroptical properties of the optically active nanofibers in organic solvents, the nanofibers were dissolved in aprotic polar solvents including NMP, DMF and DMSO. The results demonstrate that the optical activity of the nanofibers is completely lost after dissolving in these solvents. This is evident in the CD spectra taken in organic solvents where there is no longer any Cotton effect in the region corresponding to the polymer backbone except for the CD band observed at 291 nm which is associated with the CSA anion (Figure 9). In the case of NMP and DMF, because of the basic strength of these solvents, when PSBA in its emeraldine salt form is dissolved in these solvents, it becomes deprotonated and immediately produces the emeraldine base form. As a result, the chiral dopant leaves the polymer chains that in turn cause a racemization in the polymer backbone, since the emeraldine base rapidly rearranges to an achiral conformation. Bulky substituents will cause a reduction in polymer basicity strength that arises from torsional strain in the polymer backbone.[31,45,49] This phenomenon is demonstrated by UV/Vis spectra and the change in polymer color from green to blue (Figure 10). Moreover, NMP and DMF are hydrogen bond acceptors via their carbonyl oxygen which cause the hydrogen bond of the camphor sulfonate anion to the polymer backbone to be replaced by this new H-bond. The effect of NMP molecules on the structure of PSBA/HCSA is illustrated in Scheme 3. As can be seen, the basic strength of NMP causes the salt form of the polymer changing to the base form (Figure 10).
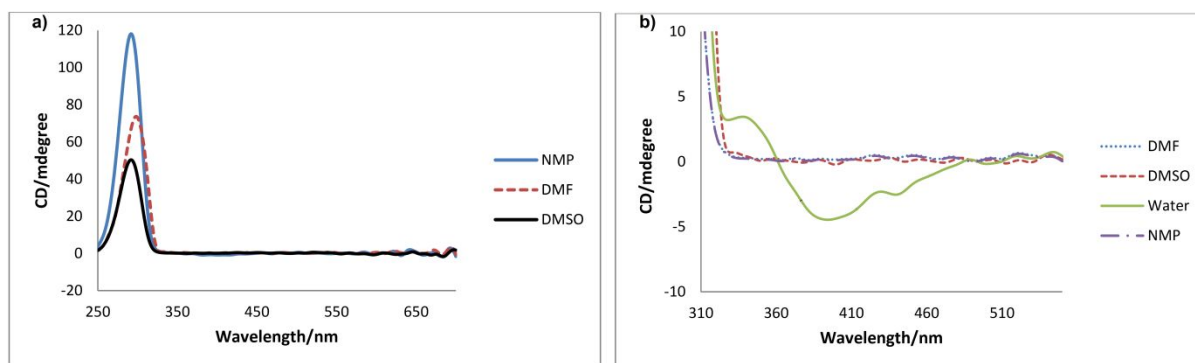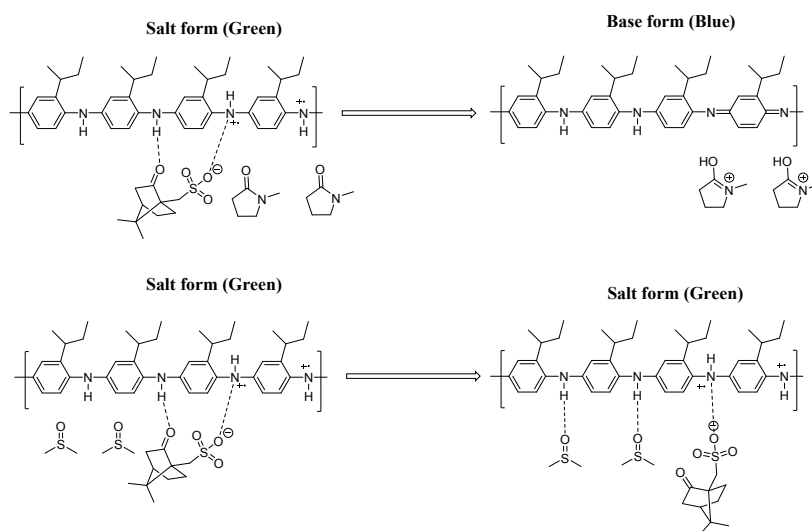
Figure 9. (a) CD spectra of optically active PSBA/(+)HCSA nanofibers dissolved in organic solvents (b) comparison of the CD spectra of the polymer dissolved in organic solvents and dispersed in water.

Scheme 3. The solvent effects of NMP and DMSO on the polymer salt form (PSBA/HCSA), the polymer in NMP solution changes to the base form (blue), but in DMSO the salt form (green) is preserved.
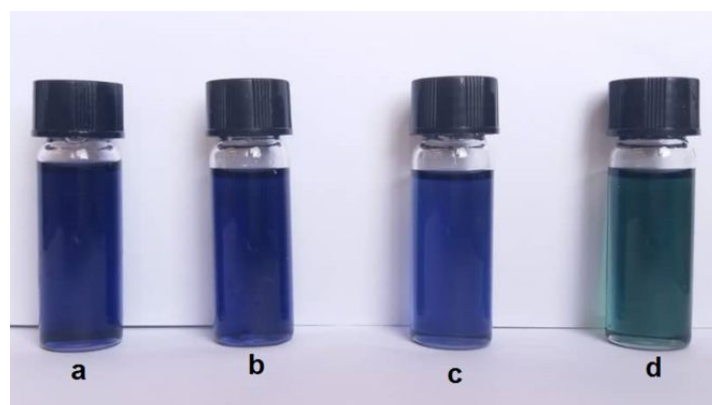

Figure 10. Photos of PSBA solutions: (a) the base form in NMP, (b) the salt form in NMP, (c) the base form in DMSO and (d) the salt form in DMSO.

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Figures 11a and 11b show UV/Vis spectra of the polymers in their salt and base forms in both NMP and DMF. Both spectra of the salt and base forms exhibit two absorption bands around 310 and 610 nm associated with π-π* and n-π* absorptions indicating similar structures in which the polymer is deprotonated.[26-30] Even when adding HCSA to the polymer solution in NMP, the color of the solution did not change to green; however, in DMF when adding HCSA the solution turned green, yet this only lasted for a few minutes after which the color changed back to blue.

However in DMSO, despite the preservation of the emeraldine salt form (as confirmed by the green colored solution and the UV/Vis spectrum, Figures 10 and 11c, respectively), the optically active PSBA/HCSA losses its chiral helical conformation as is evident in the CD spectrum (Figure 9). In fact, the CSA anion linkage with the –**HN˙⁺**– site on the polymer maintains the emeraldine salt form of the polymer, but H-bonding of the CSA carbonyl group to the polymer –**NH**– center is completely destroyed and replaced by H-bonding of the DMSO oxygen atom. This is related to the strong interaction of DMSO toward CSA due to the steric hindrance of the 2-*sec*-butyl group and the DMSO molecule being smaller than the HCSA molecule.
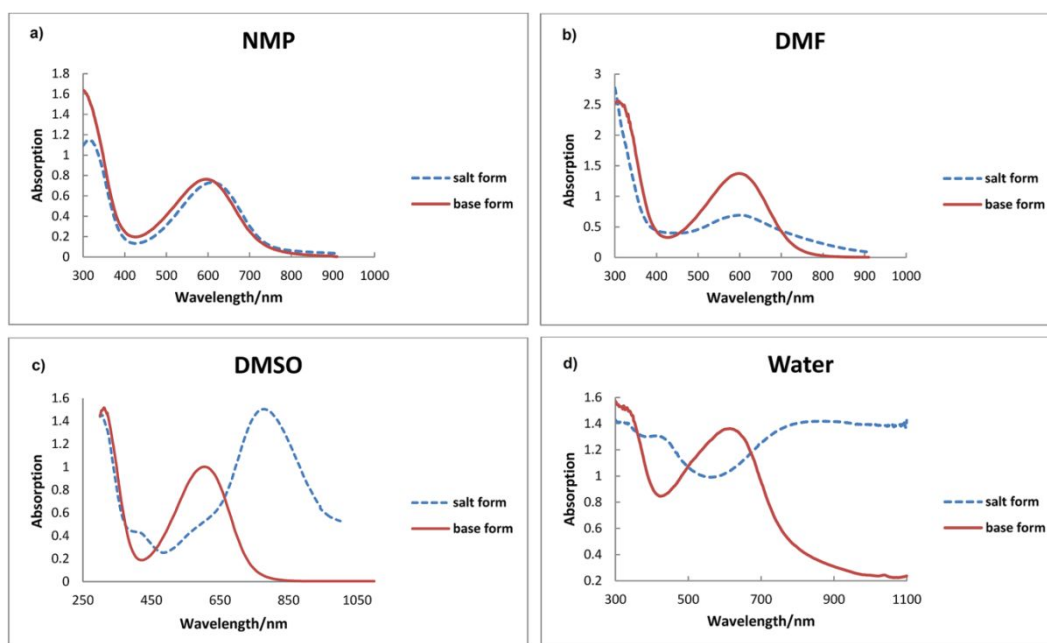

Figure 11. UV/Vis spectra of PSBA/HCSA nanofibers in base and salt forms dissolved in organic solvents: a) NMP, b) DMF, c) DMSO or d) dispersed in water.

In Figure 11c, the UV/Vis spectra of the PSBA salt and base forms are shown in DMSO. In contrast to prior solvents, the UV/Vis spectrum of the salt form in DMSO exhibits a polaron band at 785 nm along with two lower wavelength absorption bands at 310 and 425 nm that can be attributed to the benzenoid π-π* transition and a second polaron band, respectively. In addition, the UV/Vis spectrum of the base form indicates two absorption bands at 310 and 610 nm associated with the benzenoid and quinoid rings (π-π* and n-π* transitions), respectively.

Figure 12 indicates UV-Vis spectra with CD spectra together in the base and the salt forms of the optically active polymer.
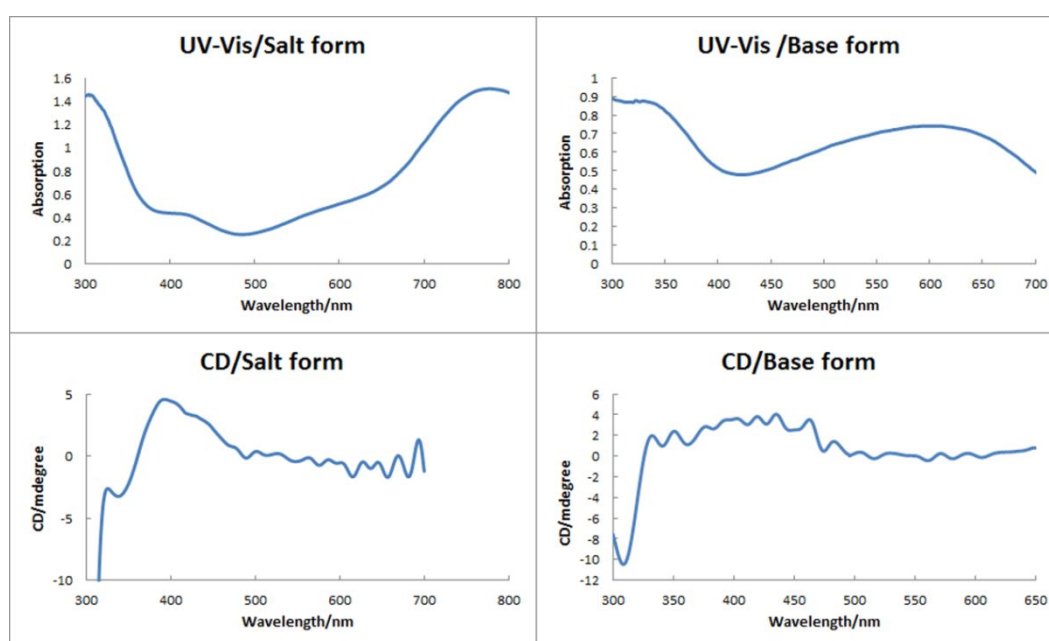

Figure 12. UV-Vis and CD spectra of the optically active polymer both in the salt and the base forms.

Previous reports indicated optically active substituted PANI such as poly(o-methoxyaniline), poly(o-ethylaniline), poly(o-toluidine) and poly(o-ethoxyaniline) preserve their optical activity in polar organic solvents such as DMF, NMP and DMSO so that the UV/Vis spectra of these polymers exhibit the emeraldine salt form.[22,25-27] However, the 2-*sec*-buthyl substituent in PSBA is too bulky so that it causes a reduction in the basic strength of the polymer.[31] Even with the addition of HCSA to the solution of the polymer in DMF and NMP, the emeraldine salt is not formed and the polymer therefore retains its base form. Consequently, the base form cannot retain a one-handed helical conformation in solution and must racemize.

Figure 11d exhibits the UV/Vis spectra of the optically active nanofibers in base and salt forms dispersed in deionized water. As can be seen, the exciton band at 638 nm indicates the polymer is de-doped. In contrast, the nanofibers in their salt form dispersed in deionized water show two bands at 324 and 416 nm associated with the benzenoid transition and the low wavelength polaron band. A broad absorption band from higher than 800 nm to the near IR region indicates a delocalized polaron free-carrier tail absorption due to the formation of the highly expanded coil chain polymer in a nanofibrillar structure. This causes the conjugation length to increase leading to higher electrical conductivity for the polymer in the nanofibrillar form than in a spherical morphology.[51-52]

Comparing the UV-Vis spectra of the nanofibers that have been dispersed in deionized water with those dissolved in an organic solvent indicates a significant difference in the conformations of the polymer chains. In fact, the polymer chains in the nanofibrillar structure possess expanded coil conformations, whereas in solution they exhibit compact coil conformations.[51-52]

Despite what is observed with PSBA/HCl, when the green emeraldine salt form of PSBA/HCSA is dispersed in deionized water, it maintains its color and the UV/Vis spectrum indicates the doped form of the polymer. In contrast, when PSBA/HCl in the salt form is dispersed in deionized water it de-dopes immediately. UV/Vis spectrum confirms this along with the color turning from green to blue. Moreover, the PSBA/H_2SO_4 doped form is stable in deionized water because the CSA$^-$ and SO_4^{2-} anions connect to the polymer chains via two bonds; a hydrogen bond to **–NH–** sites and an electrostatic bond to **–HN$^{\cdot+}$–** centers. In contrast, Cl$^-$ attaches to the polymer backbone with only an electrostatic bond and this bond is disturbed by water (Scheme 4).
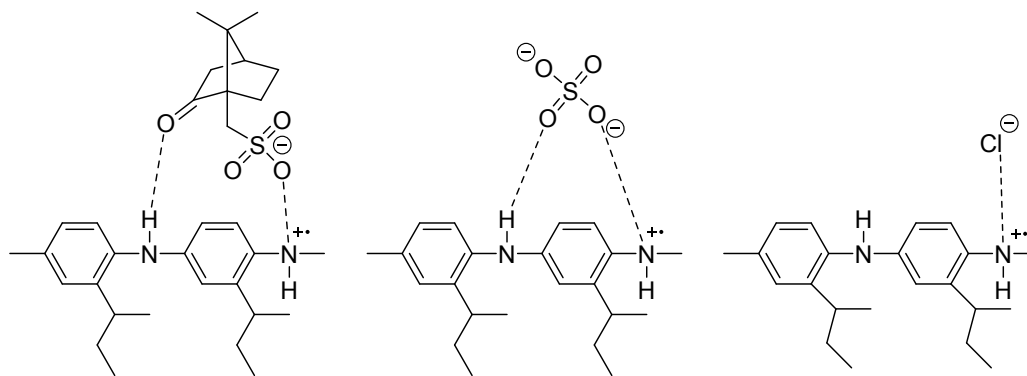
Scheme 4. The connection of CSA$^-$, SO_4^{2-} and Cl$^-$ to the PSBA backbone in the emeraldine salt form of the polymer.

Molecular weight and its distribution of the optically active nanofibers were obtained via GPC analysis. The M_n, M_w, and PDI (polydispersity index) of this polymer are 4700, 4800 and 1.02, respectively, and the data are consistent with previous reports for PANI derivatives.[15,45]

In the current study to investigate the effects of the molar ratio of APS (oxidant) to monomer on the degree of oxidation of the polymer chain, the polymerization reaction was carried out in oxidant molar ratios of 0.25, 0.375, 0.5, 0.75, 1 and 1.25 using Method 2 at a constant concentration of monomer and acid (0.025 and 1 M, respectively). The results indicate that the oxidation degree of the polymer chains is highly dependent on the molar ratio of the oxidant, which for a ratio of 0.5 molar or higher, the polymer is in its blue (salt) form indicating the polymer is more oxidized than the ideal emeraldine oxidation state (half-benzenoid/half-quinoid units).

Table 2. Effects of Oxidant Molar Ratios on Oxidation Degree of Polymer Chains*

Oxidant to monomer molar ratio	λ_{max} in base form (n→π*) dispersed in deionized water (nm)	Color of re-doped polymer solution in 0.1 M DMSO and HCSA
0.25	638	Green
0.375	626	Green
0.5	614	Blue
0.75	604	Blue
1	578	Blue
1.25	570	Blue

*At a constant concentration of monomer and acid of 0.025 and 1 M, respectively.

Therefore, the UV/Vis spectra of the de-doped polymers (base form) in water were studied[45] (Figure 13). In Table 2, n→π* absorptions of these polymers are shown. It is clear that upon increasing the molar ratio of oxidant above 0.375, the excitonic transition occurs at a lower wavelength indicating that the oxidation state of the polymer is higher than the ideal emeraldine oxidation state. This demonstrates that in this condition the oxidation state of the polymer is closer to the pernigraniline or nigraniline oxidation states. Moreover, a qualitative test for the estimation of the oxidation state of the

polymer was performed. In this test a small amount of the polymer in its base form was dissolved in a

solution of 0.1 M HCSA and DMSO. If the polymer is in its ideal emeraldine oxidation state it will

appear deep green in solution, whereas if it is in an over-oxidized state it will appear deep blue in

solution. The results of this test are shown in Table 2. As can be observed for oxidant molar ratios of

0.5 and higher, the color in solution is blue implying that the polymer is over oxidized whereas at

molar ratios of oxidant less than 0.5, the polymer is in its ideal emeraldine oxidation state because the

color of the solution turns green.
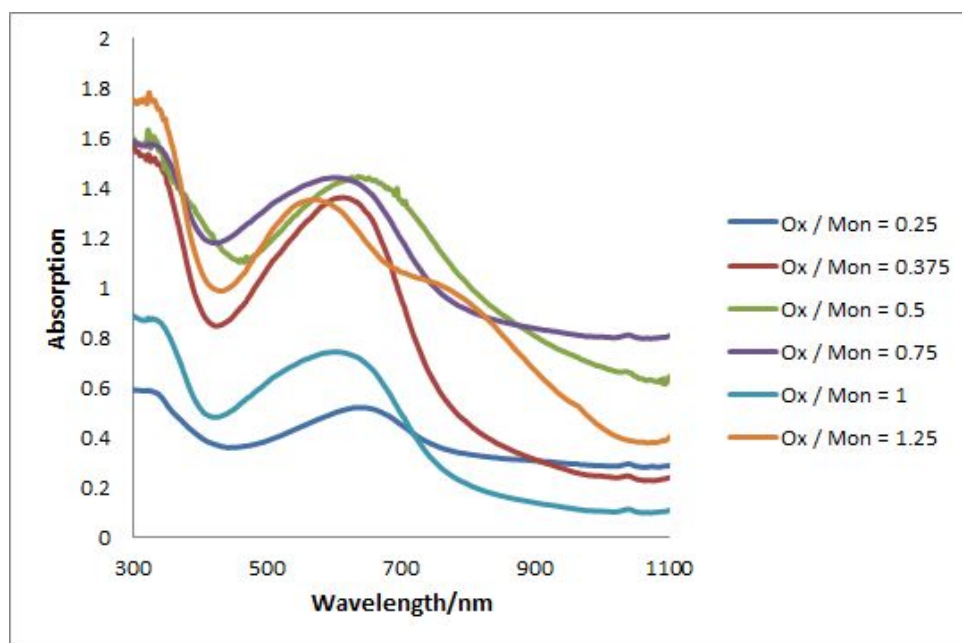
Figure 13. UV/Vis spectra of the de-doped polymers (base form) prepared under different molar ratios of APS (oxidant) to monomer in water.

Figure 14 indicates FT-IR spectra of the polymers in base and salt form, created under different

conditions. As can be seen in the doped forms, the absorption peak at 1150 cm^{-1} indicates the presence

of camphor sulfonate anion in the polymer matrix, whereas this peak is not observed in the base form.

In addition, the peak at 1315 cm^{-1} indicates that the polymer chain conformation is cisoid, providing

further evidence for a helical conformation. The absorption intensity of the two peaks at wavelengths

of 1588 cm^{-1} and 1495 cm^{-1} associated with the quantity of quinoid and benzenoid rings in the

polymer chains, respectively, indicates that the polymers are in their emeraldine or pernigeraniline

oxidation states.

The others important peaks in the FT-IR spectra of the polymers are three bands at 2872, 2928 and

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2960 cm^{-1} associated with stretching vibrations of aliphatic C-H bonds corresponding to 2-*sec*-butyl

substitution. A peak that appears about 1450 cm^{-1} is associated with the methylene C-H bond. An

important peak at about 1138 to 1142 cm^{-1} can be attributed to the doped form of the polymer. The

latter peak is accompanied by a peak around 1290 cm^{-1} that can be assigned to the **C-N$^{•+}$** form, thus

confirming the polaron state of the polymer chain in the doped form. The lack of an absorption peak

from about 1620 to 1650 indicates that cyclic phenazine has not been produced because the presence

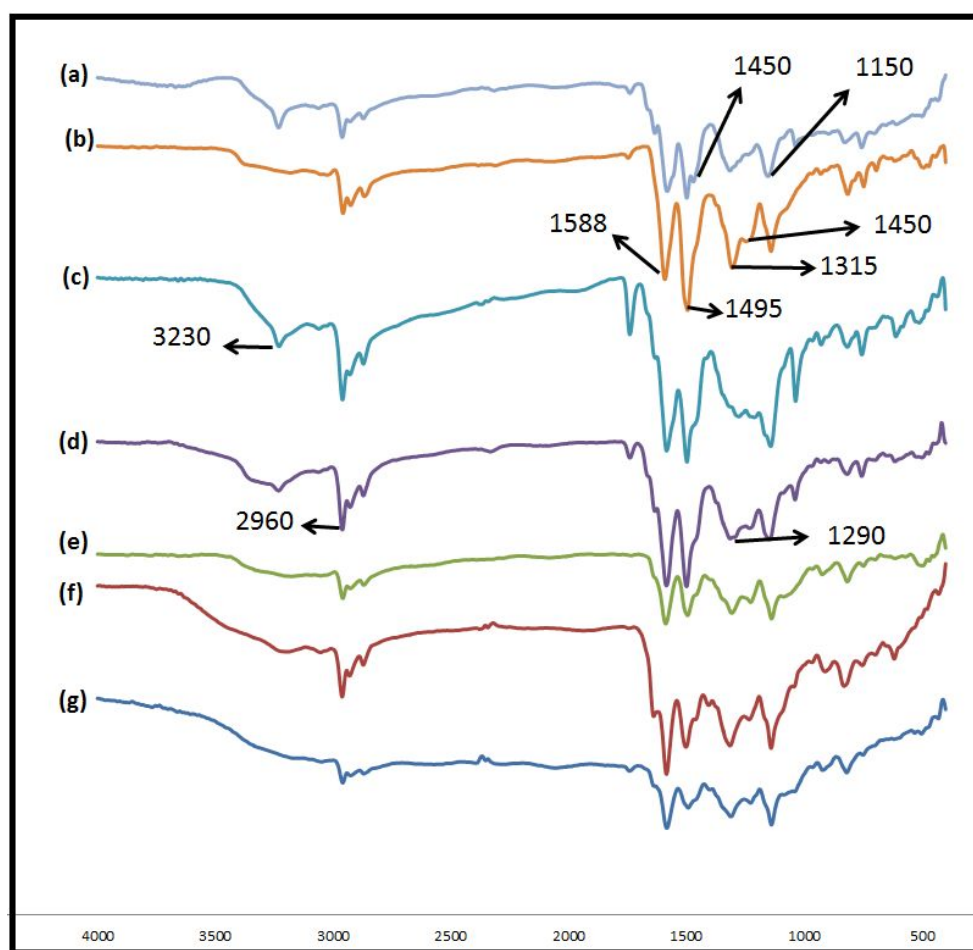of the bulky substituent, 2-*sec*-butyl likely prevents cyclic phenazine production.[33]

Figure 14. IR spectra of the polymers in base and salt forms which synthesized under various conditions at 0 °C (a) salt form, [APS]/[2SBA] = 0.25. (b) base form, [APS]/[2SBA] = 0.25. (c) base form [APS]/[2SBA] = 0.375. (d) salt form, [APS]/[2SBA] = 0.5. (e) base form, [APS]/[2SBA] = 0.75. (f) base form, [APS]/[2SBA] = 1. (g) base form, [APS]/[2SBA] = 1.25.

The electroactivity of the polymer is evident from its cyclic voltammogram (Figure 15). The

electrochemical properties of PSBA were studied by cyclic voltammetry (CV) in solution of 0.1 M

tetrabutylammonium perchlorate in the presence of a small amount of acetonitrile. The polymer in its

base form was dissolved in chloroform and cast onto a platinum electrode and tested against an

Ag/Ag$^+$ electrode as working and reference electrodes, respectively. The two anodic peaks at +0.13

and +0.718 V can be related to the conversion of the fully reduced form to the emeraldine and the

emeraldine to the fully oxidized form, respectively. The reverse peak in the reduction scan

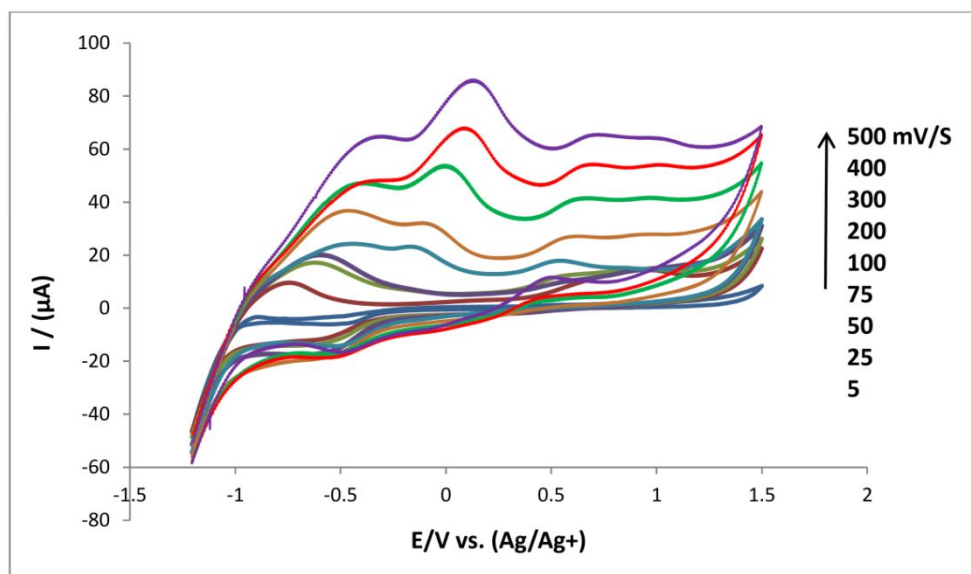demonstrates that the polymer has quasi-reversible redox properties.

Figure 15. Cyclic voltammogram of PSBA/HCSA nanofibers (Entry 7 in Table 1).

Conclusions

Unlike parent PANI, substituted PANI generates spherical structures because the substituents increase

the polymer chain flexibility. The generation of nanofibers from PANI derivatives is possible through

homogeneous nucleation via increasing the rate of the polymerization reaction by use of an initiator

with a low redox potential. The production of nanofibers even for aniline derivatives with bulky

substituents such as 2-*sec*-buthyl aniline is possible via the addition of a proper ratio of oxidant to

monomer without any agitation by a new method reported here for the first time. In addition, optically

active PSBA is created by tailoring the polymer chain helical conformation in the presence of a chiral

dopant under conditions of zero temperature, an acid dopant to monomer molar ratio about 60 and

2.5% molar initiator. Since PSBA is a bulky substituent, its basic strength is lower so that when

dissolved in an aprotic polar organic solvent the emeraldine salt form turns into the emeraldine base

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form and immediately loses its optical activity. UV/Vis spectroscopy displays a free-carrier tail absorption band from the nanofibrillar structure, when it is dispersed in deionized water, indicating that the polymer chains have an expanded coil conformation. In contrast, in solution due to the high flexibility of the chains, the polymer adopts a compact coil conformation. In addition, CV analysis indicates that the polymer is electroactive.

Methods

Materials

All materials used in this research including 2-*sec*-butyl aniline (2-SBA), N-phenyl-1,4-phenylendiamine) (NPPD), camphor sulfonic acid (HCSA), ammonium peroxydisulfate (APS) and other inorganic reagents as well as solvents were purchased from Merck Company and used as received except for 2-SBA which was distilled under vacuum prior to use.

Methods of Polymerization

Chemical oxidative polymerization of 2-SBA was carried out at 0 ℃ in the presence of either (+)- or (-)-HCSA as a chiral dopant by two methods (Method **1** and **2**). In a typical reaction 0.5 mmol of the monomer was dissolved in 10 ml of a (+)- or (-)-HCSA 1.5 M aqueous solution, then 2.5 mol% (0.0125 mmol) of NPPD as the initiator was dissolved in a minimum amount of methanol and added to the monomer solution. In another beaker 0.5 mmol of APS was dissolved in 10 ml of the same aqueous solution. The two solutions were put in a refrigerator and cooled to 0 ℃. Next the two solutions were mixed together using one of two methods. In Method **1** (according to previous reports[36-38]), after rapid mixing the two solutions, the vessel was agitated vigorously for 15 seconds and then kept at a constant temperature of 0 ℃ without stirring. However, in Method **2** (that we report here for the first time) the oxidant solution was injected by a pipette on the sidewall of the monomer vessel (within a few seconds) so that it did not cause turbulence in the monomer solution. The vessel without any agitation or stirring was placed at a constant temperature of 0 ℃. After 24 hrs, the crude product was separated by filtration and then washed adequately with deionized water. The crude polymer was dried at room temperature under vacuum for 24 hrs.

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De-doping and Re-doping

The PSBA/HCSA powder was deprotonated to give the base form of the polymer via de-protonation in NH_4OH aqueous solution. For this purpose, 40 mg of polymer salt was dispersed in 10 ml of 1 M NH_4OH and stirred for one hr and then filtered and washed with deionized water. Finally, it was dried in a vacuum desiccator at room temperature for 24 hrs.

Re-doping of the basic polymer was carried out in an organic solvent (DMSO) as well as in an acidic aqueous solution. In this regard, 1.5 mg of de-protonated polymer was dissolved in 5 ml of 0.1 M HCSA solution in DMSO and separately 10 mg of de-protonated polymer was dispersed in 5 ml of 1 M HCSA or 1 M HCl aqueous solution and stirred for one hr.

Characterization

FT-IR spectra of the doped and de-doped polymers were recorded between 400 and 4000 cm^{-1} from KBr pellets using a JASCO spectrophotometer. UV/Vis spectra of the de-doped and the re-doped polymer were recorded in organic solvents (NMP, DMF and DMSO) or deionized water at room temperature using an HACH DR 5000 spectrophotometer with concentrations of 0.03-0.08 mg/ml for solutions in organic solvents and 0.5-1 mg/ml for those dispersed in water using a 1 cm cuvette. Circular dichroism (CD) spectra of both PSBA/(+)HCSA and PSBA/(-)HCSA, as well as its base form, were obtained using a JASCO J-715 spectropolarimeter in either an organic solvent or deionized water. These samples were run at concentrations of 0.05-0.1 mg/ml for solutions in an organic solvent and 0.5-1 mg/ml for those dispersed in water using a 0.1 cm cuvette. The morphologies of the polymers synthesized under various conditions were assessed by use of a VEGA3 TESCAN scanning electron microscope (SEM). The polymer samples were covered with a thin coat of gold to improve the resolution. The molecular weight of the polymer was determined by gel permeation chromatography (GPC). A solution with a concentration of 0.2 mg/ml of the polymer in its base form in THF (tetrahydroforan) was provided, then 20 μl of the solution was injected into the column at 25 °C. Cyclic voltammetry (CV) analysis was performed in a range of -1.5 to +2 volts with a scan rate of 5 to 500 mv/s). The electrochemical properties of PSBA were studied by cyclic voltammetry (CV) in solution of 0.1 M tetrabutylammonium perchlorate in the presence of a small

amount of acetonitrile. The polymer in its base form was dissolved in chloroform and cast onto a platinum electrode and tested against an Ag/Ag$^+$ electrode as the working and reference electrodes, respectively.

Acknowledgements

Declaration of interest

The authors declare no competing financial interest.

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