Synthesis and Characterization of Poly(*n*-undecyl isocyanate)/Polyaniline Polyblend

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Received 7 May 2008; accepted 8 November 2008
DOI 10.1002/app.29727
Published online 2 March 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Poly(*n*-undecyl isocyanate) (PUDIC)/*n*-dodecylbenzenesulfonic acid (DBSA)-doped polyaniline (PANIDBSA) polyblend was prepared and the effect of the H-bonding between these two polymers on the compatibility, conjugation chain length of PANIDBSA, and helixity of PUDIC in the polyblend system were studied. The monomer and polymer were characterized by NMR spectra and the polyblend was analyzed by FTIR, UV–vis spectra, and wide-angle X-ray diffraction. It was found when the blend composition of the PUDIC was higher than 10%, the WAXD patterns demonstrated lower angle shifting for the peaks at around $2\theta = 2$–2.5°, referring to the distance between the layers of the layered structure of PANIDBSA crystalline with increasing PUDIC, indicating the expansion of the layered structure of PANIDBSA. The FTIR spectra illustrated the presence of an absorption peak at 1700 cm^{-1} shift to higher wave number with PUDIC due to its H-bonding with PANIDBSA. The UV–vis spectra of PANIDBSA described a blue-shift of the λ_{max} with PUDIC, indicating that the presence of PUDIC in the polyblend system can interrupt and decrease the conjugation chain length of PANIDBSA. The optical activity of the helical PUDIC decreased notably with the presence of PANIDBSA, resulting from the reversed helical effect (de-nature) of H-bonding. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1–7, 2010

Key words: blends; chiral; conducting polymers

INTRODUCTION

Intrinsically conducting polymers (ICP) are useful for a large number of applications: conducting paints and glues, electromagnetic shielding, antistatic formulations, sensors and actuators, electronic devices, and corrosion protection are a few examples.[1,2] ICP included polyparaphenylene (PPP), polypyrrole (PPy), polythiophene (PTh), and polyaniline (PANI) etc. Su and Kuramoto[3] report the use of long alkyl organic acid (ex: *n*-dodecylbenzenesulfonic acid (DBSA) to be the dopant[3–5] can avoid polyaniline chain curl and increase its solubility on common organic solvents.

Shashoua et al.[6–8] reported the using of NaCN as the initiator in preparing a helical poly(alkyl isocyanate) (nylon 1) in N,N-dimethylformamide (DMF) via the low temperature (-100°C to 40°C) anionic polymerization. These kind of polymers own rigid backbones of length ~ 40 nm,[9,10] due to the conjugation of the carbonyl π electrons to C—N bonding. Goodman[11] synthesized poly(alkyl isocyanates) having optical activity due to the helical conformation at -78°C but the product has low yield and broad molecular weight distribution. Muller and Zental[12,13] describe the synthesis of seven new types of copolymer series prepared by copolymerization of hexyl isocyanate with seven new chiral azo chromophores with an isocyano functionality. The resulted copolyisocyanates (Nylon 1) have a good solubility but the yield is still low. The above methods were concerned about the synthesis of various nylon 1 to study either their solubility in common organic solvents or the chirality of their solution. This research is to synthesize one of the nylon 1, poly(*n*-undecyl isocyanate) (PUDIC) to study the possibility of destroying its helical conformation through the formation H-bonding between its carbonyl groups and other H-donating polymer by polyblend. Once the H-bonding through the carbonyl group is formed, its π electron will not be able to conjugate with backbone C—N group. The loss of backbone conjugation (rigidity) can reduce the possibility for nylon 1 to create a helical conformation or even become a random-coiled polymer. The removal of its helical conformation can be checked from the decrease of its chirality in the solvent and is similar to the so-called de-nature (disappearance of helical conformation) behavior of a biopolymer when its

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intramolecular H-bonding was destroyed at high temperature (i.e. frying).

To increase the probability of the formation of H-bonding, we used DBSA-doped polyaniline (PANIDBSA) which also has long alkyl side chains and H-donating amine group to blend with PUDIC. Therefore, we can analyze the conformational change of the PUDIC with the effect of the formation H-bond and its compatibility with PANIDBSA. It would be very interesting if the chirality of the PUDIC in the blend can be sensed simply by measuring the conductivity or λ_{max} of the blend, which is also related to the composition.

And, on the PANIDBSA part, we can study the change of its length of conjugation by the red or blue shift of its λ_{max}, which is also related to the degree of extension (random-coil or extended) of its backbone before and after mixing with PUDIC.

EXPERIMENTAL

Preparation of PANIDBSA by emulsion polymerization

The 0.13 mol of aniline monomer was mixed in a solution of 0.0027 mol SLS, 0.0644 mol DBSA, and 160 g of deionized (DI) water in four-necked flask equipped with a mechanical stirrer and stirred for 1 h to allow the formation of an emulsion solution. The 20 mL of fuming sulfuric acid was added slowly to the previous solution to obtain an emulsion solution of anilinium salt monomer. APS (0.01 mol) was dissolved in 30 mL of water and was added to the solution to carry out the emulsion polymerization overnight. The micelle droplets with obtained polymers were destroyed to release the enclave polymers by the addition of *n*-butylacetate and kept stirring for 20 min. The organic phase with PANIDBSA was then separated from water by a funnel. Large amount of methanol was poured into the organic phase to precipitate the PANIDBSA from *n*-butylacetate. The mixture was filtered to obtain the filter cake which was then washed with methanol mixed until the filtrate became colorless. The cake was then dried at 60°C for 24 h in an oven.

Synthesis of *n*-undecylisocyanate

n-undecylisocyanate was prepared as follows: 0.1 mol distilled lauroyl chloride (Aldrich, USA, ACS grade) was mixed with 0.12 mol sodium azide (Aldrich) in 250 mL dry toluene (dried with sodium and collected followed by distillation) and refluxed overnight. The unreacted sodium azide and the by-product sodium chloride were separated by vacuum distilling the *n*-undecylisocyanate out. A distillate with a bp at 80–85°C (vacuumed to 800 Pa) was collected and the yield is estimated to be around 29%.

Polymerization of PUDIC[14,15]

250 mL of Dimethylformamide (DMF, Aldrich, ACS grade) was placed into a 500-mL three-necked flask with 1 g phosphorous pentoxide (P_2O_5) for overnight and then distilled with a bp at 38°C and 400 Pa. Sodium cyanide was dried in vacuum with P_2O_5 for 4 h, dissolved in the dry DMF (in a 10-mL volumetric flask) to make a saturated solution. A 100-mL flask was dried on flame and inert gas (Argon) was purged through the system. The temperature was kept at −36°C by a dry ice/acetone bath. Thirty milliliters of DMF was injected into the flask and 1 mL of undecylisocyanate, 10 min later. After 20 min, one drop of the saturated sodium cyanide solution of DMF was injected into the batch, a white cluster of polymer suddenly appeared in the solution. Excess methanol was poured into the mixture to terminate the polymerization.

The polymer was isolated by filtration and about 0.3 g of white powder was obtained. This product was further purified by dissolution in chloroform, precipitation by methanol, and drying in vacuum. 0.23 g of PUDIC was obtained with a yield of 23%.

Preparation of PUDIC/PANIDBSA

2.5 wt % PANIDBSA and 0.5 wt % PUDIC were prepared in xylene solution individually by dissolving the dry polymers in the solvent and was stirred for at least 24 h. PUDIC/PANIDBSA with various percentages of PUDIC (0.5, 1, 2, 5, 10, and 20%) were prepared by mixing these two different solutions together in various proportions. Some of the solution was kept to be analyzed by UV–vis and optical activity meter, the rest was dried at 60°C for 24 h for other measurements.

Characterization

Nuclear magnetic resonance (NMR)

^{1}H-NMR spectrum of *n*-undecylisocyanate monomer was obtained from its deuterated chloroform solution using a Bruker MSL-300 spectrometer operated at 300 MHz. And PUDIC dissolved in the deuterated chloroform (conc. 1 mg/1 mL) was used to obtain its ^{13}C-NMR spectrum from a Varian Gemini 300 MHz NMR spectrometer. Chemical shifts were referenced to ^{13}C signals of the deuterated solvent.

Fourier transform infrared spectroscopy (FTIR)

The IR spectra of all the samples were obtained from a Bio-Rad FTS 165 FTIR with a resolution of 4 cm^{-1}

and 16 scanning mixed and stapled into tablet with dry KBr powders. The scanning wave numbers ranged from 4000 to 400 cm^{-1}. The IR spectra of lauroyl chloride, *n*-undecylisocyanate, PUDIC, and PANIDBSA were recorded.

Optical activity

The optical activities of neat PUDIC and PUDIC/PANIDBSA were obtained from a Polax-D Type optical meter.

UV–vis spectroscopy

The UV–vis spectra of the various polyblend in solution were obtained from a Hitachi U-2000 at 200 nm/min. The scanning wave length ranged from 1100 nm to 600 nm.

Wide-angled X-ray diffraction (WAXD)

A Phillips X-ray generator was used for the X-ray diffraction studies. Samples were cast on the slide or just placed on the slide. The samples were exposed to a Cu/Ni targeted radiation with 45 kV and 35 mA from 2° to 40°, the exposure time of 50 s in every 0.04° was used.

RESULTS AND DISCUSSION

NMR spectra

^{1}H-NMR spectrum of the synthesized product from the reaction of azide with acyl chloride in refluxing toluene proved to be *n*-undecylisocyanate as shown in Figure 1 which demonstrates several types of

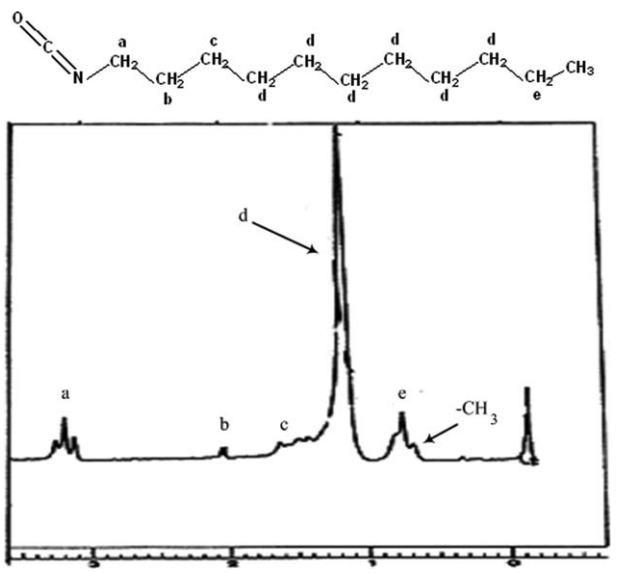


Figure 1 ^{1}H-NMR spectrum of *n*-undecyl isocyanate monomer.

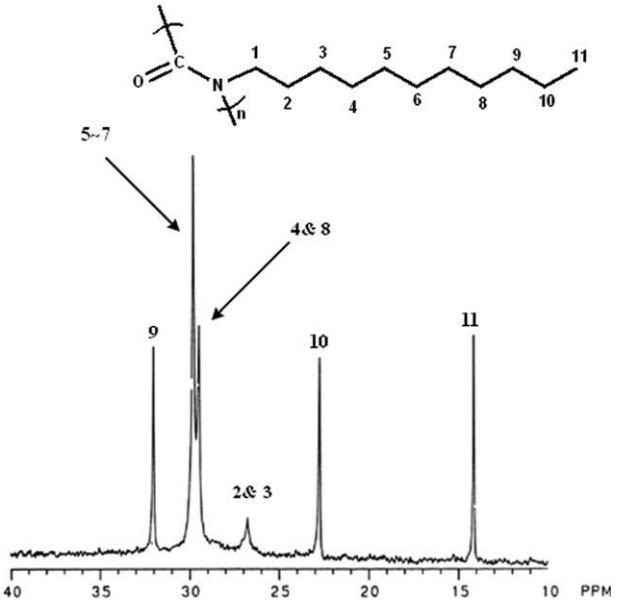


Figure 2 ^{13}C-NMR spectrum of PUDIC.

methylene —CH_2—, and methyl —CH_3 groups of the alkyl *n*-undecyl chain. ^{13}C-NMR spectrum shown in Figure 2 was used to characterize the PUDIC in *d*-$CHCl_3$. The assignment of the resonance peaks of various carbons are illustrated in the attached chemical structure. The resonance peaks of the aliphatic carbons of *n*-undecyl side chain can be seen around 10–40 ppm from Figure 2 except the carbonyl carbon whose absorption peak is at 52 ppm and not demonstrated in the spectrum. From the characterization on the monomer and polymer by NMR spectra, a helical, rigid poly(alkylisocynate) is prepared.

IR spectra

The IR spectrum of the lauroyl chloride which is the precursor of *n*-undecylisocyanate monomer was illustrated in Figure 3(a) with a huge absorption at 1800 cm^{-1} assigned as the carbonyl group of the acyl chloride. It was converted into isocyanate by Curtis rearrangement after refluxing with sodium azide in dry toluene with nitrogen gas released during reaction. Then, it was found in Figure 3(b) that the acyl chloride group at 1800 cm^{-1} disappeared entirely and isocyanate groups at 2200 cm^{-1} appeared after the formation of *n*-undeylisocyanate which was then polymerized by NaCN in DMF into PUDIC, demonstrating a strong carbonyl band at 1700 cm^{-1} in Figure 3(c). The *n*-undecyl side chain remained unchanged during the preparation of isocyanate and polymerization as seen from Figure 3(a–c). And Figure 3(d) revealed the presences of both the quinoid and benzenoid ring of neat PANIDBSA from the absorption peaks at 1559 and 1478 cm^{-1}, respectively. The absorption band at 1300 cm^{-1} of the C—N on both the

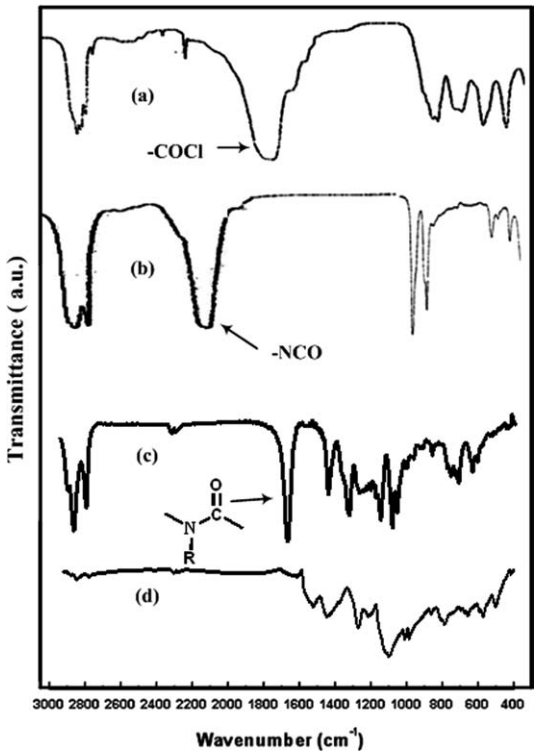


Figure 3 IR-spectra of (a) lauroyl chloride, (b) *n*-undecyl isocyanate, (c) PUDIC, (d) PANIDBSA.

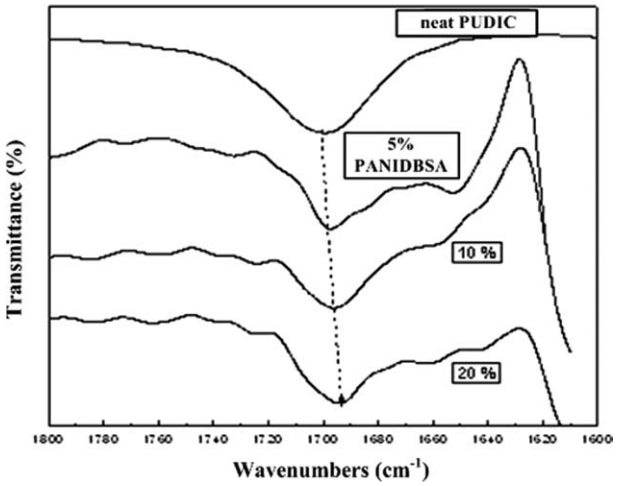


Figure 4 IR-spectra of PUDIC with increasing PANIDBSA in the blends.

PANIDBSA and PUDIC backbone is very significant, and the absorption peaks at 1005 and 1030 cm^{-1} characterize the —S=O belonged to the $-SO_3H$ group of PANIDBSA. All assigned peaks were listed in Table I.

The absorption peak at 1700 cm^{-1} representing the stretch mode of the —C=O was used to monitor the interaction between PANIDBSA and PUDIC in the blends. In Figure 4, the carbonyl shifted to higher wave number due to the increase of the stretching strength of —C=O bond after blending with small amount of PANIDBSA in toluene, indicating the presence of the hydrogen bonding with the PUDIC as the H-acceptor (carbonyl) and PANIDBSA as the H-donator (amine). The strong H-bonding was able to induce the reversing of the helical conformation of PUDIC as depicted in Scheme 1 and effectively depressed the overall optical activity of PUDIC in toluene since the R (+) and D (−) circulation will cancel each other.

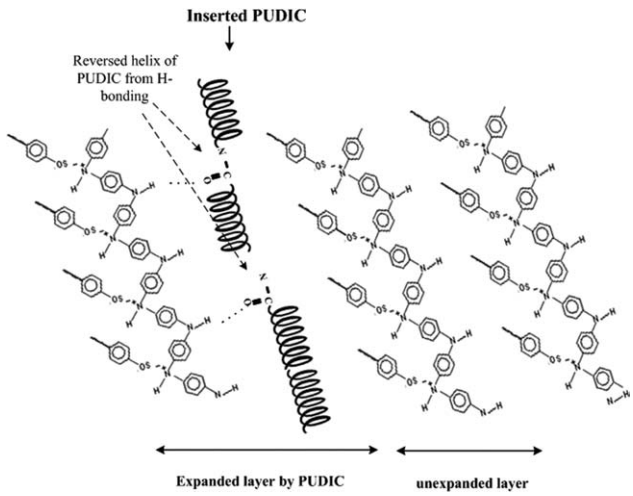
TABLE I
Assignments of IR Spectrum of PANIDBSA

Frequency (cm^{-1})	Assignment
2958	ν (—CH_3)
2924	ν (—CH_2—)
1600	ν (—C=C—), benzene ring
1561	doped ν (—C=N—) of quinoid
1467	doped ν (—C=C—) of benzoid
1307	ν (—C—N—)
1178	H^+N=⟨⟩=N^+H
1135	—B—NH—B—
1034	ν_{as} (—S=O) of $-SO_3H$
1006	ν_{sy} (—S=O) of $-SO_3H$
801	ν (C—H) para-substituted aromatic out of plain bending

X-ray diffraction patterns

The full span of WAXD patterns for all neat polymers and polyblends were shown in Figure 5 with a compact hexagonal cylindrical structure of the rigid rod packing.[16]

The hairy rod structure of rigid polymers with long alkyl side chains easily demonstrates a self-organized layer-to-layer structure with alkyl side



Scheme 1 schematic diagram of H-bonding between PUDIC and PANIDBSA with reversing helical conformation of PUDIC.

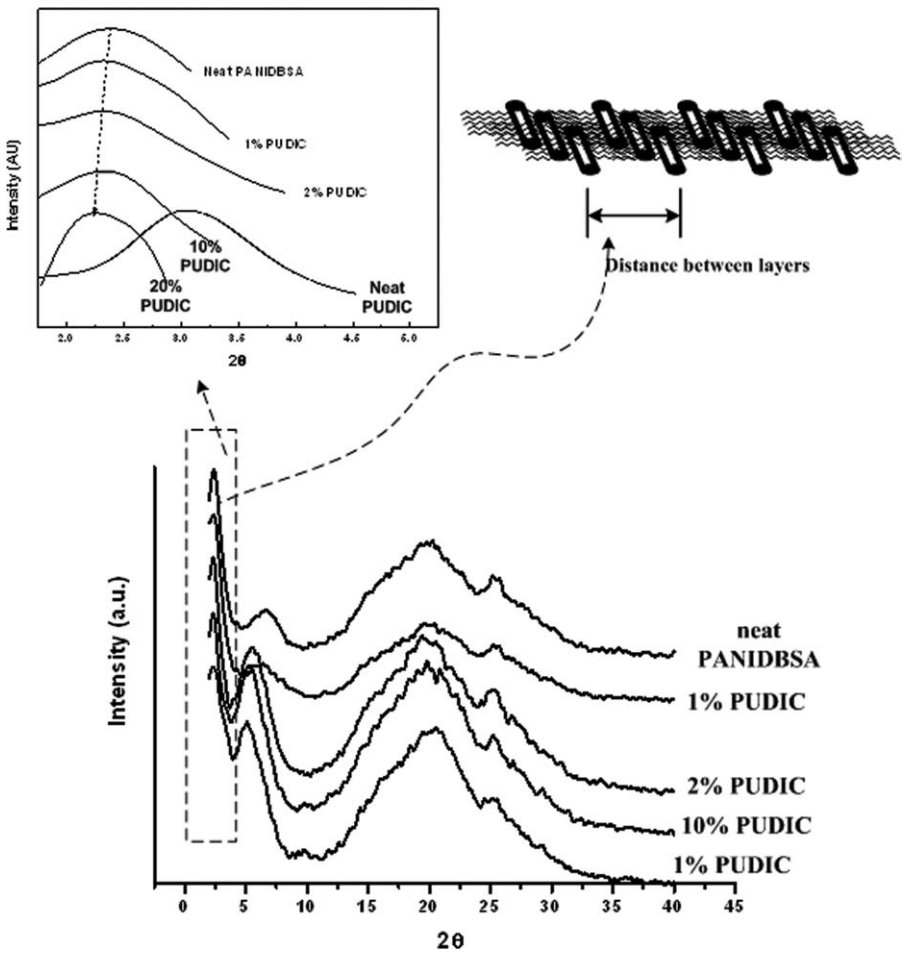


Figure 5 Wide angled x-ray diffraction patterns of PANIDBSA with increasing PUDIC in the blends.

chains interdigitized to each other and the layer-to-layer distance can be determined from the diffraction angles (2θ) around 2–5° from its WAXD pattern.[16–22] Both PANIDBSA and PUDIC demonstrated the layered structure with significant diffraction peaks at low angles (2–5°) from which the layer-to-layer distance created from the extension of their nonpolar long alkyl side chains described in the upper right graph in Figure 5 can be obtained. To characterize the possible structural variation of the layered structure of PANIDBSA in the blend, the X-ray diffraction patterns of blends with various thermal compositions were taken and shown in the upper left graph in Figure 5. The distances between the layers were calculated from the diffraction peak at $2\theta = 2.35°$ which is corresponding to 3.74 nm for neat PANIDBSA and $2\theta = 3.26°$ corresponding to 2.71 nm for neat PUDIC, respectively. As there are only 11 carbons of *n*-undecyl side chain for neat PUDIC, illustrating a length of 2.71 nm which is shorter than 3.74 nm of phenyl-*n*-dodecyl side chains of PANIDBSA with a phenyl and twelve numbers of carbons. The PANIDBSA created a diffraction peak of (002) at smaller angle (~ 2–2.5°), representing the layer distance of PANIDBSA were interfered by the introduction of small amount of PUDIC. When more and more PUDIC were incorporated into the polyblend system, the diffraction peak shifted to lower angle, indicating the expansion of layer distance of PANIDBSA due to the insertion of PUDIC, resulting from the formation of H-bonding between these two polymers as described in Scheme 1. When the blend ratio were increased to be over 10%, the lower angle shifting was more significant due to the increase of the compatibility.

UV–vis spectra

Various compositions of PUDIC/PANIDBSA were taken by UV–vis spectroscopy and shown in Figure 6. Commonly, the doped polyaniline would produce a localized polaron, resulting in a λ_{max} around 750–850 nm, referring to the conjugation length of PANIDBSA backbone. Now, the PANIDBSA had a λ_{max} at 827 nm and the peak experienced a blue-shift with rising ratio of PUDIC. When the ratio of PUDIC was raised to 20%, the λ_{max} shifted from 827 to 812 nm due to the gradually increasing

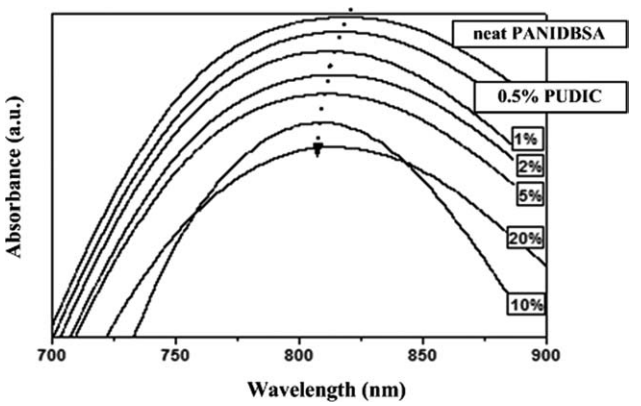


Figure 6 UV–vis spectra of PANIDBSA with increasing PUDIC in the blends.

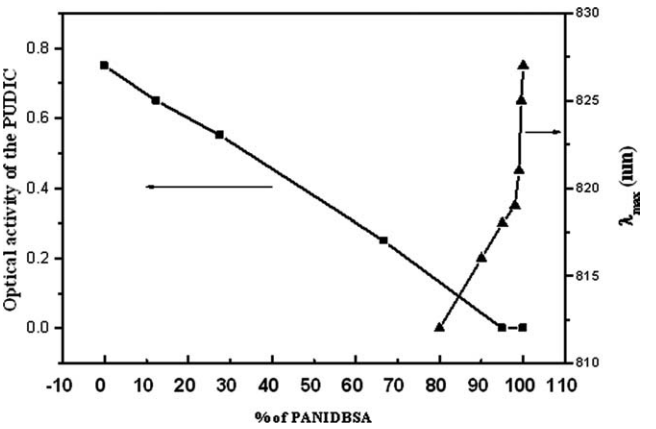


Figure 7 Diagram of optical activity and max versus composition of PANIDBSA.

interruption on the conjugation length of PANIDBSA by PUDIC through the formation of the H-bonding between them.

The normalized conductivity (apparent conductivity divided by composition) is provided to replace apparent one to remove the effect of dilution of nonconducting material of PUDIC in the blends. When normalized conductivities of various PUDIC/PANIDBA were calculated and listed with λ_{max} in Table II, it is found that the conductivities of PANIDBSA dropped with PUDIC composition as were the values of λ_{max}. The intermolecular H-bonding from PUDIC did contribute to the decreasing conductivity through the re-coiling on the PANIDBSA, which also led to the blue shift of λ_{max}.

The H-bonding in the blends brought PUDIC closer to the PANIDBSA and the bulky alkyl side chain of PUDIC can cause the re-coiling of the PANIDBSA structure through the so-called reverse secondary doping effect, which enhanced the blue shift.[20]

Optical activity

The H-bonding can also change the degree of helical conformation of PUDIC itself, which can be monitored by comparing the optical activity of neat PUDIC and polyblends. As both the conjugation chain length of PANIDBSA and optical activity of PUDIC depend strongly on the formation of H-bonding, in Figure 7 the optical activity and λ_{max} versus the composition of PANIDBSA was plotted to illustrate their relationship. The optical activity of the helical PUDIC decreased notably with the presence of PANIDBSA, resulting from the H-bonding due to the reverse, (de-natured) helical effect on the helical conformation of the PUDIC as seen in Scheme 1. The helical, reverse effect came from the losing of conjugation along the PUDIC backbone when the lone paired electrons of carbonyl groups were not able to conjugate with the main-chain C—N bonds after being occupied by the H-donating amine groups through the formation of the H-bonding.

TABLE II
λ_{max} and Conductivity of Various PUDIC/PANIDBSA

PUDIC/ PANIDBSA	λ_{max} (nm)	Apparent conductivity (s/cm)	Normalized conductivity (apparent conductivity/ composition of PANIDBSA) (s/cm)
0/100	827	0.61	0.61
0.5/99.5	825	0.60	0.60
1/99	824	0.51	0.51
2/98	821	0.47	0.48
5/95	818	0.32	0.34
10/90	816	0.12	0.13
20/80	812	0.08	0.1

CONCLUSIONS

This research was based on synthesizing PUDIC that has a long alkyl side chain attaching to a helical rod structure to blend with PANIDBSA. The interaction of the polyblend system was found to originate from the formation of the H-bonding between the carbonyl groups of PUDIC and amine groups of PANIDBSA. The WAXD patterns indicated the distance of lamellar structure of PANIDBSA backbone and were expanded with PUDIC from the insertion of it due to the formation of H-bonding. The presence of H-bonding was illustrated by the higher wave number shifting of the absorption peak at 1700 cm^{-1} characteristic of the —C=O of PUDIC with the introduction of PANIDBSA. The hydrogen bonding between PUDIC and PANIDBSA also contributed to the blue shift of the λ_{max} of UV–vis spectra due to the decreased conjugation length of PANIDBSA backbone. The optical activity of the helical PUDIC decreased notably with the presence of PANIDBSA, resulting from the de-naturing (reverse helix) effect of the helical conformation of the PUDIC.

The formation of intermolecular H-bonding effect on the component polymers with helical conformation and high conjugation turns out to be very interesting. In the future, a nanorod polyaniline will be prepared and will be mixed with the helical rod PUDIC to study the compatibility, rigidity, helixity of the rigid polymer blend.

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