Effect of Aniline-Formaldehyde Resin on the Reduced Conjugation Length of Doped Polyaniline: Thermal Studies

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ABSTRACT: A linear aniline-formaldehyde resin (AF) complexed with different acids was successfully synthesized with the traditional way of polymerizing a novolac-type phenolic resin. When the $AF(DBSA)_{1.0}$ (AF complexed with only HDBSA (*n*-dodecyl benzene sulfonic acid)) was blended with $PANI(DBSA)_{0.5}$ (polyaniline doped only by HDBSA, the T_gs (glass transition temperatures) of the polyblends decreased with $PANI(DBSA)_{0.5}$, indicating the presence of the compatibility that can alter the doping condition of $PANI(DBSA)_{0.5}$ by changing the conjugation length. In the polyblend system, it was also confirmed when the polyblend of 50/50 showed a higher residue weight than the rest of polyblends after being heated up to 450°C. The λ_{max} of UV–vis spectra of PANI $(DBSA)_{0.5}$ demonstrates a red shifts indicating the secondary doping effect (increasing conjugation length) was recovered when $PANI(DBSA)_{0.5}$ was mixed with less than 50% of $AF(DBSA)_{0.5}$ $(HCl)_{0.5}$. Similar phenomenon of red shift was found for the blended samples of $PANI(DBSA)_{0.5}$/$AF(DBSA)_{1.0}$ at high temperatures. IR spectra revealed an alkyl affinity interaction is present between $PANI(DBSA)_{0.5}$ and $AF(DBSA)_{1.0}$ at room temperature and a strong and free localized polaron band appeared at high temperatures due to the recovery of secondary doping. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2120–2128, 2007

Key words: aniline-formaldehyde; polyaniline; polyblend

INTRODUCTION

Polyaniline, especially doped polyaniline, has attracted much attention during the last decades due to its easy way of synthesis, good environmental stability, and high conductivity compared to regular polymers. However, the solubility of polyaniline in a regular organic solvent is pretty poor due to the drastically increased solubility parameter,[1] which makes the procession of polyaniline impossible. It was reported that through protonation with HDBSA (*n*-dodecyl benzene sulfonic acid), polyaniline can be both conductive and soluble in many common nonpolar or weakly polar organic solvents.[2–3] The long alkyl chain of doped DBSA (*n*-dodecyl benzene sulfonate), acting as a plasticizer, provides polyaniline with bulky space, improving the miscibility of polyaniline-based polyblend system[3–4] and making the processing or blending possible. The doping of polyaniline by

protonic acid is called "primary doping." MacDiarmid and Epstein[5] defined another doping behavior that can also increase conjugation length (the appearance of a free carrier tail in a UV-spectrum) without protonation, as "secondary doping." The role of the secondary dopant is to destroy the H-bonding between polyaniline molecules by creating a strong interaction with the polyaniline backbones, or the primary dopants, and subsequently increases the conjugation by a more extended structure. It was found that the conformation of the polyaniline backbones changes from a "coiled" structure to an extended one with the incorporation of secondary dopants.[6–7] Ho[8] illustrated that a secondary dopant obtained from polymerizing phenol with formaldehyde can form a H-bonding with polyaniline backbones and demonstrate a higher λ_{max} than that of $PANI(DBSA)_{0.5}$ due to the increase of conjugation chain length and the presence of a more extended backbone.

The blending of $PANI(DBSA)_{0.5}$ with other matrix polymers[9–14] can put an effect on the conjugation length of $PANI(DBSA)_{0.5}$ by the polymeric secondary doping effect if the matrix polymers have benzene rings with H-bondable functional groups. AF (aniline-formaldehyde) resin is the best choice for the matrix polymer, not only for its benzene structure with

H-bondable functional groups, but also for using the same aniline monomer as the polyaniline. However, AF(DBSA)$_{1.0}$ turned out to be a unfavorable effect that reduced the conjugation length of polyaniline chains. It is shown that the introduction of this interaction related with DBSA brings a reduced conjugation length of DBSA-doped polyaniline, which can be monitored by the blue shifting of the localized polaron band of polyaniline in UV–vis spectra.

The influences of temperature on the miscibility and conjugation of polyaniline with AF(DBSA)$_{1.0}$ (DBSA-complexed aniline-formaldehyde with an equivalent mole ratio of DBSA and aniline) will be checked with high-temperature UV–vis and IR-spectra, thermal analysis, and X-ray diffraction patterns. This study will try to examine the cause of the reduced conjugation length of the polyaniline prepared in a blend with aniline formaldehyde resin as the concentration of the DBSA related compounds is increased.

EXPERIMENTAL

Synthesis and sample preparation

Preparation of PANI(DBSA)$_{0.5}$

Similar to regular emulsion polymerization,[15] 12 mL aniline, 21 g HDBSA (behaving as both dopants and emulsifiers), 160 mL distilled water were mixed and mechanically stirred in a 250 mL four-necked flask in a ice-bath with purging nitrogen gas. The polymerization was initiated dropwise with an ammonium peroxodisulfate aqueous solution. To avoid a rise of the reaction temperature during polymerization, polymerization was initiated by a very slow drip of ammonium peroxodisulfate aqueous solution at 0–5°C, which lasted for at least 24 h. The obtained polyaniline was then precipitated out in acetone bath, followed by filtration, and the filtered cake was washed with excessive acetone to remove the residue HDBSA and dried in vacuum at 40°C for 24 h. The obtained polyaniline is named as PANI(DBSA)$_{0.5}$.

Preparation of AF(DBSA)$_x$(HCl)$_y$

Aniline formaldehyde resin was obtained by polymerizing aniline with formaldehyde in the presence of acids[16,17] (HDBSA and HCl). An acid (HDBSA or HCl) was first complexed with 93 g aniline in a 1000-mL four-necked flask with slow stirring by a magnetic stirrer, and a 29.2 g 37% formaldehyde aqueous solution was slowly dropped into the mixture by a funnel. And the reaction temperature was increased to 80°C, followed by introducing 19.4 g formaldehyde solution and 300 mL distilled water. Then, the reaction temperature was gradually raised to 90–100°C and stayed for 4 h with the opening of the flask cover to remove the excess or condensed water to obtain a higher mole-

cular weight aniline formaldehyde resin. The obtained AF(DBSA)$_x$(HCl)$_y$, where "x" and "y" refers to the *feed mole ratio* of HDBSA and HCl, respectively, with aniline, was dissolved in acetone and added dropwise into stirring water bath to remove residual acids. The precipitate was isolated and dried in a vacuum oven at 35°C until no weight loss was found, which took several days.

Polymer blending

The 5% PANI(DBSA)$_{0.5}$ and 10% AF(DBSA)$_x$(HCl)$_y$ xylene solutions were prepared, respectively, and mixed together to make a polyblend solution. Various volume ratios of each polymer solution with constant concentration (5% PANI(DBSA)$_{0.5}$ and 10% AF(DBSA)$_x$(HCl)$_y$) were prepared and mixed together to make samples with different solid weight ratios of DBSA-doped polyaniline and AF(DBSA)$_x$(HCl)$_y$, i.e., when solvent was evaporated the blend is in weight ratio. The polyblend solution was stirred for 24 h, followed by casting on a petri dish and dried in the vacuum oven at room temperature for at least 24 h.

Characterization and measurements

Electron spectroscopy for chemical analysis

The chemical structure of AF(DBSA)$_x$(HCl)$_y$ were analyzed by an ESCA instrument of Fison(VG)-ESCA-LAB 210 using Al Kα X-ray source at 1486.6 eV. The pressure in the chamber was maintained under 10^{-6} Pa or lower during the measurement. A tablet sample was prepared by a stapler. The binding energies of the N$_{1s}$ around 400 eV were recorded.

^{1}H-NMR spectroscopy

^{1}H-NMR spectra for characterization of AF(DBSA)$_x$(HCl)$_y$ was obtained in a deuterated chloroform solution using a Bruker MSL-300 spectrometer operated at 300 MHz.

Solid-state ^{13}C-NMR

Solid-state ^{13}C-NMR experiments were performed with a Bruker AVANCE-400 spectrometer, equipped with a Bruker double-tuned 7 mm probe. The ^{13}C chemical shifts were externally referenced to tetramethylsilane (TMS).

Modular DSC analysis

About 8 mg of neat or blended sample was subjected to a modular DSC analysis (MDSC) of TA-2920 and heated at 10°C/min from 0 to 120°C, in purging N$_2$.

Thermogravimetric analysis

Neat and blended samples were given a thermal gravimetric analysis (TGA) by a TA SDT-2960 at 20°C/min, under purging N_2.

High temperature UV–vis spectroscopy

The UV–vis spectra of the samples were obtained from a Hitachi U-2000. The wavelength ranged from 1100 to 400 nm, and only the wavelength covering visible light was demonstrated (600–1100 nm). The samples were prepared by dipping a thin glass plate into a polyblend solution, followed by drying at room temperature for about 24 h. For obtaining high temperature data, the glass plate was clamped inside a hot-stage and put in front of the light source of a U-2000 and heated at 10°C/min from room temperature to 220°C.

High temperature FTIR spectroscopy

The IR-spectra of various samples were obtained from a Bio-Rad 165 FTIR with a resolution of 4 cm^{-1}, and by 16 scannings in dry KBr. The scan ranged from 4000 to 400 cm^{-1}. For high temperature data, the sample was clamped inside a hot-stage and put in front of the IR source and heated at 10°C/min from room temperature to 220°C.
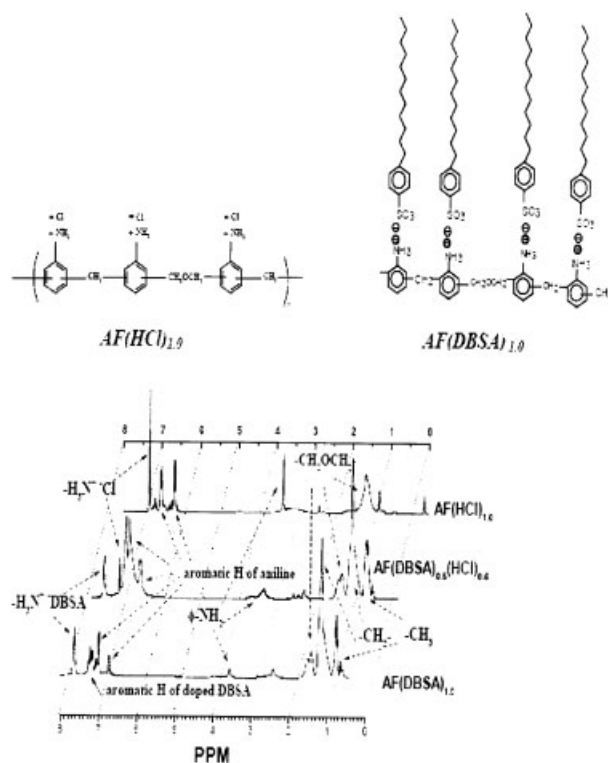
RESULTS AND DISCUSSIONS

ESCA spectroscopy

The N_{1s} core-level spectra of the AF(DBSA)$_x$(HCl)$_y$ revealed the presence of two types of structures corre-
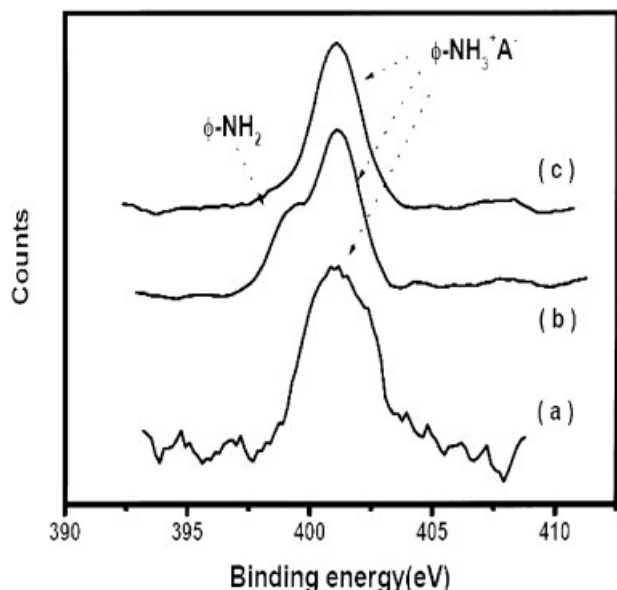
Figure 1 ESCA spectra of (a) AF(DBSA)$_{1.0}$; (b) AF(DBSA)$_{0.5}$ (HCl)$_{0.5}$; (c) AF(HCl)$_{1.0}$.
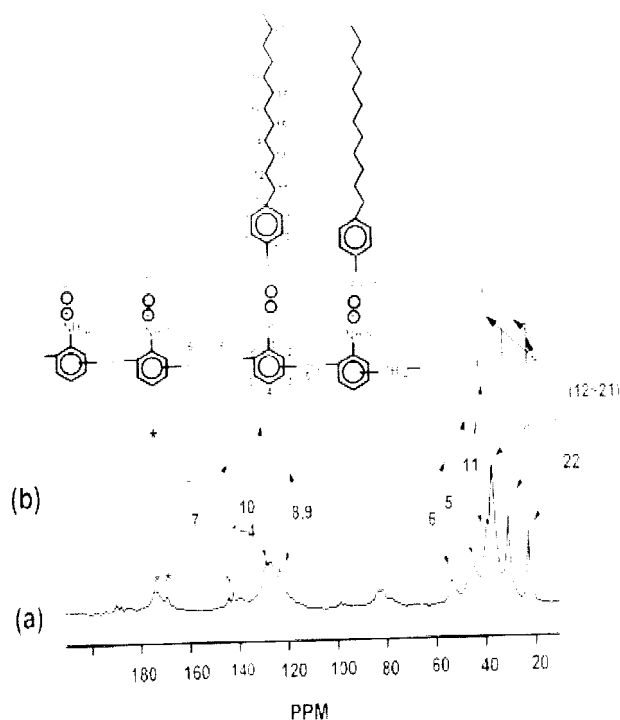
Figure 2 ^{1}H-NMR spectra of AF(DBSA)$_x$(HCl)$_y$.

sponding to the binding energy peaks at 401.5 and 399.2 eV, respectively. They can be assigned to be the nitrogen atoms of the complexed aniline (Φ-NH$_3^+$A$^-$) and free aniline units (Φ-NH$_2$) of the corresponding aniline formaldehyde resins, respectively. Only complexed aniline units were found for both AF(DBSA)$_{1.0}$ and AF(HCl)$_{1.0}$ as shown in Figures 1(a and c), implying the fully complexed structures from HDBSA or HCl and no free aniline units were left. However, some of free aniline units were found when AF was prepared in a mixed acid of equal moles of HDBSA and HCl as shown in Figure 1(b).

^{1}H-NMR spectroscopy

The ^{1}H-NMR spectra of AF(DBSA)$_x$(HCl)$_y$ ($x = 1.0$; $y = 0$; $x = y = 0.5$; $x = 0$; $y = 1$) are shown in Figure 2, displaying the resonance peaks of the aliphatic protons of complexed DBSA and AF(DBSA)$_x$(HCl)$_y$ backbones at $\delta = 0.65$, 0.78, 1.18, and 1.43 ppm. Etheryl and amine protons (noncomplexed free aniline units) are displayed at $\delta = 1.57$ and 3.56 ppm, respectively. The protons of ammonium are at 7.85 (with DBSA$^-$ counter ion) and 7.34 ppm (with Cl$^-$ counter ion),[18] respectively. It seems that the integrated area of the characteristic peak of DBSA$^-$ counter ions is larger than that of Cl$^-$ ones, which indicate that x may be larger than y-value. The aromatic protons linked with sulfo-group demonstrate signals at $\delta = 7.23$ ppm, the

Figure 3 Solid-state ^{13}C-NMR spectra of (a) AF(DBSA)$_{1.0}$; (b) AF(DBSA)$_{0.5}$(HCl)$_{0.5}$.

TABLE I
Assignments of AF(DBSA)$_x$(HCl)$_y$ FTIR-Spectra

Frequency (cm^{-1})	Assignment
3500–3300	ν(—N—H of ⬡—NH$_2$ or ⬡—NH$_3^\ominus$)
2960′2850	ν_{as} and ν_{sy} (—CH$_3$), could not be found for **AF(HCl)$_{1.0}$**
2920	ν(—CH$_2$—), could not be found for **AF(HCl)$_{1.0}$**
1600	ν(—C=C—), benzene ring
1600–1575	δ(—N—H of ⬡—NH$_3^\ominus$)
1470	δ(—CH$_2$—)
1370–1250	ν(—C—N—)
1034	ν_{as}(—O=S=O) of —SO$_3$H, could not be found for **AF(HCl)$_{1.0}$**
1006	ν_{sy}(—S=O) of —SO$_3$H, could not be found for **AF(HCl)$_{1.0}$**
912	(o,o′, p)-substitution
820	p- and (o,p)-substitution
756	o-substitution

rest protons of benzene rings belonged to aniline formaldehyde backbones exhibited signals at $\delta = 7.20$, 7.00, 6.75 and 6.74 ppm, respectively.

Solid-state ^{13}C-NMR

The spectra of solid-state ^{13}C-NMR of neat AF(DBSA)$_{1.0}$ and AF(DBSA)$_{0.5}$HCl$_{0.5}$ are shown in Figure 3. The related carbon resonance positions of spectra are illustrated with the attached functional groups. The aliphatic carbons peaks of DBSA of AF(DBSA)$_{1.0}$ and AF(DBSA)$_{0.5}$HCl$_{0.5}$ can be seen around 20–40 ppm in both Figures 3(a and b). The methylene carbons of neat AF(DBSA)$_{1.0}$ and AF(DBSA)$_{0.5}$HCl$_{0.5}$, which linked benzene rings, were located at 45 and 55 ppm. The benzene-ring carbons of both aniline and DBSA were approximately located at 120–140 ppm. Basically, solid-state NMR spectrum of neat AF(DBSA)$_{1.0}$ resembled to that of neat AF(DBSA)$_{0.5}$HCl$_{0.5}$ since the substitution of DBSA with Cl ions does not change the resonance of any carbons.

FTIR spectroscopy

The absorption peaks of AF(DBSA)$_x$(HCl)$_y$, listed in Table I, revealed the presence of stretching (3500–3300 and 1006, 1034 cm^{-1}) modes of alkyl and sulfonic groups of DBSA respectively, for both AF(DBSA)$_{1.0}$ and AF(DBSA)$_{0.5}$(HCl)$_{0.5}$, that were not found for AF(HCl)$_{1.0}$. The bending (1600–1575 cm^{-1}) mode of

complexed aniline with acids was found for each sample. Except for the ideal ortho- and ortho-linking (756 cm^{-1}), ortho- and para- (912 and 820 cm^{-1}) polymerization of aniline with formaldehyde in the presence of acids can be seen from the spectra assignment listed in Table I.

DSC analysis

Evidence about the presence of an interactive force between PANI(DBSA)$_{0.5}$ and AF(DBSA)$_{1.0}$ was issued from the shifting of glass transition temperatures (T_g) of AF(DBSA)$_{1.0}$ in the blends. The DSC thermograms of PANI(DBSA)$_{0.5}$/AF(DBSA)$_{1.0}$ were given in Figure 4 and the T_gs are listed in Table II. We can demonstrate the presence of compatibility from the
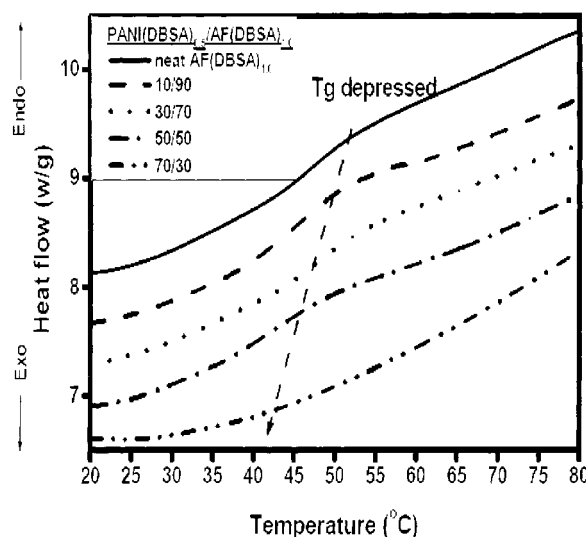
Figure 4 DSC thermograms of PANI(DBSA)$_{0.5}$/AF(DBSA)$_{1.0}$.

TABLE II
Thermal Data of PANI(DBSA)$_{0.5}$/AF(DBSA)$_{1.0}$

PANI(DBSA)0.5/ AF(DBSA)1.0	T_g (°C) of AF(DBSA)1.0	Plateau residue WEIGHT % after 450°C
Neat PANI(DBSA)$_{0.5}$	–	31.6
90/10	–	31.0
70/30	–	30.8
50/50	42	30.6
30/70	46	23.5
10/90	46	18.6
Neat AF(DBSA)$_{1.0}$	48	16.7

variation of the T_gs of the AF(DBSA)$_{1.0}$ in the blends compared with that of neat AF(DBSA)$_{1.0}$. The T_g of the AF(DBSA)$_{1.0}$ in the polyblend decreased with PANI(DBSA)$_{0.5}$ due to its plasticizing effect. When more than 50% PANI(DBSA)$_{0.5}$ was added, the depression of T_g became more significant due to an effective plasticization and better compatibility. The compatibility between PANI(DBSA)$_{0.5}$ and AF(DBSA)$_{1.0}$ derived from the affinity of DBSA of each component and resulted in the blue shift of λ_{max} and the reduced conjugation length.

Thermogravimetric analysis

The interaction between PANI(DBSA)$_{0.5}$ and AF (DBSA)$_{1.0}$ changed the degradation behavior of the PANI(DBSA)$_{0.5}$/AF(DBSA)$_{1.0}$ polyblend as well. The degradation behavior of neat PANI(DBSA)$_{0.5}$, AF(DBSA)$_{1.0}$, and blended samples were characterized via TGA. According to Figure 5, neat AF(DBSA)$_{1.0}$ and PANI(DBSA)$_{0.5}$ were found to gradually decomplex and dedope at temperature higher than 220°C[19] due to the debonding (decomplexation or dedoping) of DBSAs from the main chains of AF(DBSA)$_{1.0}$ and PANI(DBSA)$_{0.5}$, respectively. The AF(DBSA)$_{1.0}$ turned out to be an aniline-formaldehyde (AF) free of HDBSA and the PANI(DBSA)$_{0.5}$ became the nonconductive emeraldine base (EB) at high temperature. The noncomplexed AF went on to further degrade into stable 4,4′methylene dianiline, the precursor of 4,4′methylene diisocyanates (MDI) used in the preparation of polyurethane,[20] and resulted in a weight loss plateau even after 450°C as shown in Scheme 1. EB continued crosslinking[19,21] and demonstrated a plateau curve after 450°C. It was found that the final residual weights of neat PANI(DBSA)$_{0.5}$ and AF(DBSA)$_{1.0}$ reached a plateau value at 31.6% and 16.7%, respectively. The residual weights of the polyblend after 450°C are listed in Table II. Interestingly, the residual weight of polyblends of 50/50 list in Table II is quite different and goes higher from the rest, indicating the presence of an interactive force between PANI(DBSA)$_{0.5}$ and AF(DBSA)$_{1.0}$ in the polyblend. The residual weight for 50/50 was also

found to demonstrate a bigger T_g depression from that of neat AF(DBSA)$_{1.0}$. Of course, the higher residual weight is possible due to the change of the decomposition pathways with the interaction that may result in a chemical reaction (nonphysical) between two polymers.
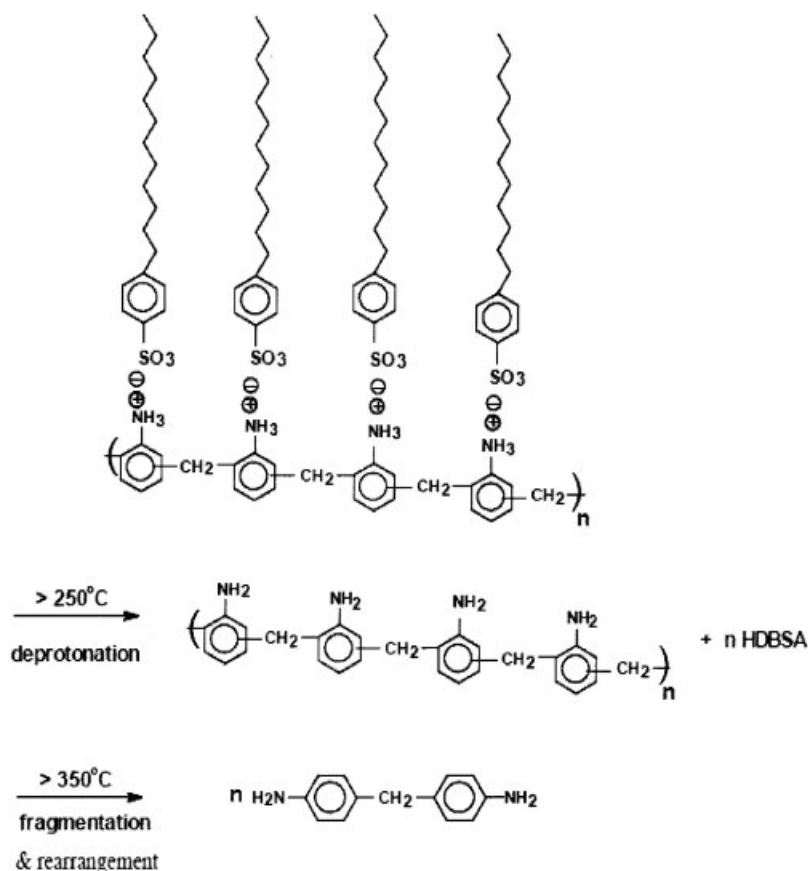
High temperature UV–vis-spectra

It was found that polyaniline synthesized in the presence of excess HDBSA had a maximum absorbance wavelength (λ_{max}) at 775 nm, and after being washed with acetone, the PANI(DBSA)$_{0.5}$ was found to have a λ_{max} at 878 nm, much higher than that of unwashed DBSA-doped polyaniline.[22]

The reduced conjugation length from DBSA can also be found when PANI(DBSA)$_{0.5}$ is mixed with DBSA-complexed aniline formaldehyde (AF(DBSA)$_{1.0}$). The presence of AF(DBSA)$_{1.0}$, with a lot of complex DBSA, behaved like residual DBSA to interrupt the conjugation of PANI(DBSA)$_{0.5}$ backbones by polyblending.[22] Theoretically, aromatic chemicals, or polymers such as phenolic resin[8] with H-bonding group can remove the polarization effect of the counter ions that complexed to the polyaniline main chains and improve the conjugation, which is the so called secondary doping effect. On the contrary, AF(DBSA)$_{1.0}$ having aniline and amino groups demonstrated a reduced conjugation length due to the shielding from the complexed DBSA which kept the aniline away from polyaniline backbones, and aggravated the reduced conjugation length by its interaction with the doped DBSA of PANI(DBSA)$_{0.5}$. The presence of complexed DBSA in AF(DBSA)$_{1.0}$ is still necessary since they can guaranteed not only the dissolution of AF(DBSA)$_{1.0}$ in xylene[23] but improve the compatibility with PANI(DBSA)$_{0.5}$.

The reduced conjugation length can be also avoided by less amount of complexed-DBSA when less AF was complexed with HDBSA before polymerization with formaldehyde. A AF(DBSA)$_{0.5}$(HCl)$_{0.5}$ was pre-
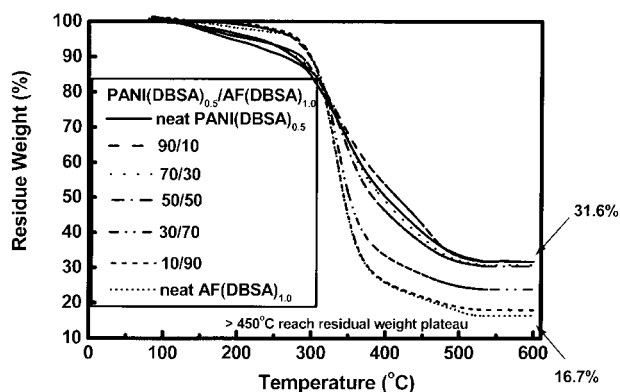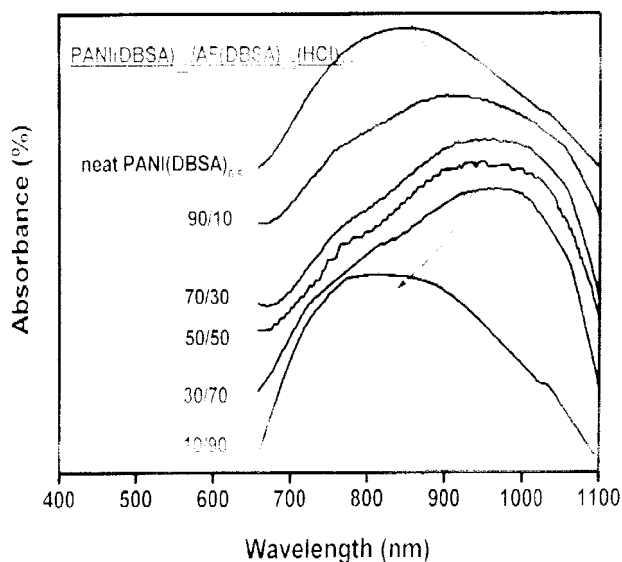

**Figure 5** TGA thermograms of PANI(DBSA)$_{0.5}$/AF(DBSA)$_{1.0}$.

Scheme 1 High temperature deprotonation and fragmentation of AF(DBSA)$_{1.0}$.

pared in the presence of equal moles of HDBSA and HCl and was blended with PANI(DBSA)$_{0.5}$ in the same way like PANI(DBSA)$_{0.5}$/AF(DBSA)$_{1.0}$. When UV-spectra of PANI(DBSA)$_{0.5}$/AF(DBSA)$_{0.5}$(HCl)$_{0.5}$ were taken, we found λ_{max} increase (red shift) when

AF(DBSA)$_{0.5}$(HCl)$_{0.5}$ is below 50% as shown in Figure 6(a–d), which is totally different from those of PANI(DBSA)$_{0.5}$/AF(DBSA)$_{1.0}$ (blue shift) and the secondary doping effect is recovered for aniline-formaldehyde (AF) resin. Obviously, AF(DBSA)$_{0.5}$(HCl)$_{0.5}$ that has only 50% of complexed DBSA behave like a polymeric dopant[8] without the interruption (shielding) of complexed DBSA. In other

Figure 6 UV–vis spectra of PANI(DBSA)$_{0.5}$/AF(DBSA)$_{0.5}$ (HCl)$_{0.5}$.
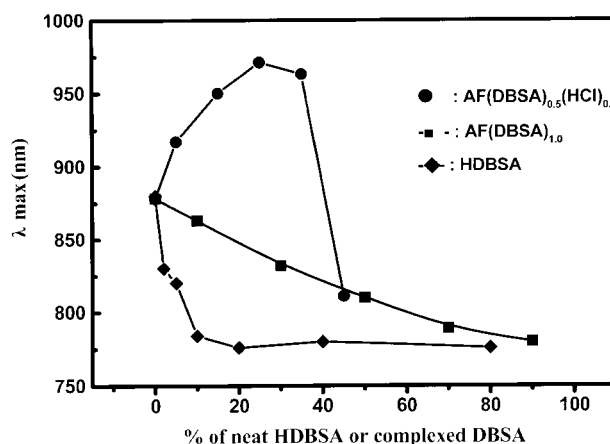
Figure 7 λ_{max}s of PANI(DBSA)$_{0.5}$ and PANI(DBSA)$_{0.5}$/ AF(DBSA)$_{1.0}$ versus neat HDBSA or complexed DBSA.
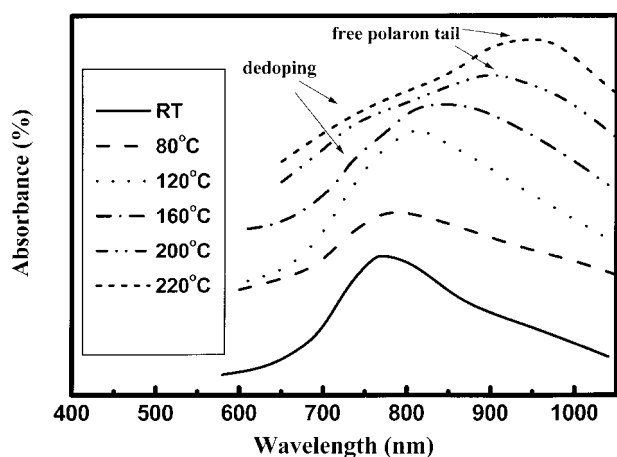
Figure 8 High temperature UV-spectra of 10/90 PANI (DBSA)$_{0.5}$/AF(DBSA)$_{1.0}$.

words, the conformation of AF(DBSA)$_{0.5}$(HCl)$_{0.5}$ is much like a rigid rod compared to AF(DBSA)$_{1.0}$, which allowed the aniline groups of AF(DBSA)$_{0.5}$(HCl)$_{0.5}$ to come closer to the backbone of PANI(DBSA)$_{0.5}$ to induce the so-called secondary doping effect and straightened its molecular chain to obtain a higher λ_{max} (better conjugation). However, the reduced conjugation length occurred again when too many complexed DBSAs were present in the polyblend when composition of AF(DBSA)$_{0.5}$(HCl)$_{0.5}$ is over 50%, resulting in a decreasing λ_{max} (blue shift) from Figure 6(d–f).
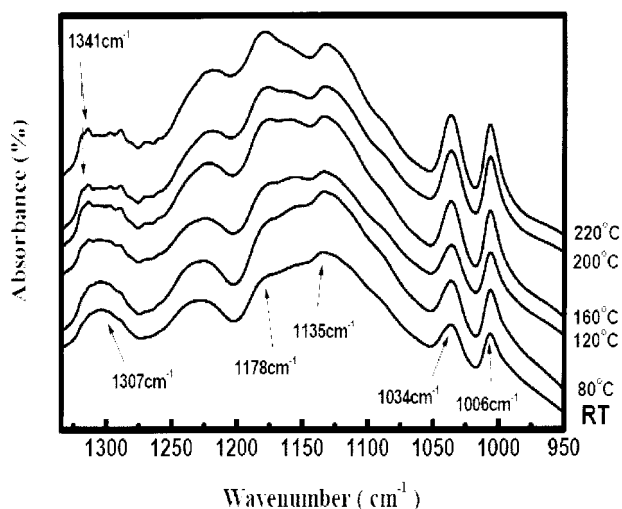
The quantitative comparison of the reduced conjugation length from excess HDBSA and complexed DBSA of AF(DBSA)$_{1.0}$ and AF(DBSA)$_{0.5}$(HCl)$_{0.5}$ can be made by comparing the λ_{max} at the same HDBSA or complexed DBSA composition when mixed with PANI (DBSA)$_{0.5}$ according to Figure 7. When neat HDBSA is replaced by the complexed DBSA belonging to AF(DBSA)$_{1.0}$, the effect was significantly depressed. The difference of λ_{max} decreased with the DBSA com-

position and slight difference can still be seen when 90% of AF(DBSA)$_{1.0}$ is mixed with PANI(DBSA)$_{0.5}$. Obviously, the complexed DBSA of AF(DBSA)$_{0.5}$ (HCl)$_{0.5}$ did not behave like neat HDBSA. The λ_{max} increased tremendously with less than 25% of complexed DBSA in AF(DBSA)$_{0.5}$(HCl)$_{0.5}$ (50% of AF (DBSA)$_{0.5}$(HCl)$_{0.5}$ in the polyblend) but decreased abruptly to the same position with that of AF(DBSA)$_{1.0}$ with 45% of complexed DBSA in AF(DBSA)$_{0.5}$(HCl)$_{0.5}$ (90% of AF(DBSA)$_{0.5}$(HCl)$_{0.5}$ in the polyblend).

The interruption of the conjugation by complexed DBSA can be alleviated by a thermal perturbation. Theoretically, the thermal motion decreases the conductivity by interfering with the conjugation, resulting in the blue shift of λ_{max}. Surprisingly, the shielding effect of complexed DBSA (DBSA attaching to AF(DBSA)$_{1.0}$ itself) on AF(DBSA) can be removed at high temperature. Figure 8 and Table III illustrated that the λ_{max} (at around 780 nm) of PANI(DBSA)$_{0.5}$ in 10/90 PANI(DBSA)$_{0.5}$/AF(DBSA)$_{1.0}$ at room temperature was red-shifting with temperature to a wavelength even higher than that of neat PANI(DBSA)$_{0.5}$. A λ_{max} in the near-IR range (>900 nm) was caused by a formation of a polaron tail (a free localized polaron band). And the red shift of the λ_{max} could be enhanced at temperatures over 220°C according to Figure 8. Briefly, the movements of λ_{max} from 780 to 943 nm when temperature was increased from room temperature to 220°C are listed in Table III. The appearance of the secondary doping effect at elevated temperature may have come from the close proximity of aniline groups of AF(DBSA)$_{1.0}$ to PANI(DBSA)$_{0.5}$ molecules due to the deshielding of the complexed DBSA from high temperature. A dedoping effect from the losing of the doped DBSA for PANI(DBSA)$_{0.5}$ itself can be seen from the presence and growing of the peak around 700 nm in Figure 8 at temperatures higher than 160°C. The

TABLE III
Various Localized Polaron Band of λ_{max} (nm) of PANI(DBSA)$_{0.5}$/AF(DBSA)$_{1.0}$,
PANI(DBSA)$_{0.5}$/HDBSA, and High-Temperature λ_{max} of 10/90
PANI(DBSA)$_{0.5}$/AF(DBSA)$_{1.0}$

	PANI(DBSA)$_{0.5}$/ AF(DBSA)$_{1.0}$	PANI(DBSA)$_{0.5}$/ HDBSA	10/90 of PANI(DBSA)$_{0.5}$/AF(DBSA)$_{1.0}$
10/90	780		780 (RT)
20/80		776	
30/70	789		790 (80°C)
40/60		780	
50/50	810		815 (120°C)
70/30	832		844 (160°C)
80/20		776	
90/10	863	784	
95/5		820	
98/2		830	
100/0	880	880	
			900 (200°C) > 880 (neat)
			943 (220°C) > 880 (neat)

Figure 9 High temperature IR-spectra of 10/90 PANI (DBSA)$_{0.5}$/AF(DBSA)$_{1.0}$.

growing peak around 700 nm is due to the absorption of π–π^* transition of the nonconductive EB type of polyaniline. The source of the recovery of the secondary doping effect at high temperatures can be determined by IR-spectra with the functional group point of view.

High temperature FTIR-spectra

The thermal perturbation effect on the conjugation length of the doped polyaniline can also be attributed to the functional interaction as characterized by vibrational spectra at higher temperatures. The IR-spectra of PANI(DBSA)$_{0.5}$/AF(DBSA)$_{1.0}$ with ratio of 10/90 were obtained at various temperatures to analyze the thermal effect. Figure 9 illustrates that the doublet peaks of asymmetric and symmetric stretches of sulfo-groups at 1034, 1006 cm^{-1} became sharper as the temperature rose from room temperature. These peaks indicate that DBSA molecules become softer at higher temperatures and can no longer deter the approaching aniline groups of AF(DBSA)$_{1.0}$ to PANI(DBSA)$_{0.5}$ backbones. We also found that the absorption peak of 1178 cm^{-1} of the H$^+$N$=\underset{}{\bigcirc}=N^+$H bipolaron group grew with temperature, illustrating that more bipolarons appeared at high temperature. That is why the absorbance of λ_{max} representing the localized polaron band decreased with temperature as can be seen from Figure 8. Moreover, the free (unbonded) —C—NH— (1307 cm^{-1}) of PANI(DBSA)$_{0.5}$ splits into several peaks at high temperatures (>80°C) as shown in Figure 9 The additional peak at 1341 cm^{-1} represents a possible bonding related to —C—NH— group. It showed that the recovery of the secondary doping effect at high temperatures was caused

by the interaction involved the release of the —C—NH— of PANI(DBSA)$_{0.5}$.[8]

CONCLUSIONS

The DBSA that complexed to AF(DBSA)$_{1.0}$ contributed to the miscibility with PANI(DBSA)$_{0.5}$ and also induced the decrease of the conjugation length of PANI(DBSA)$_{0.5}$. The reduced conjugation length from the compatibility can be confirmed by the depression of the T_gs of AF(DBSA)$_{1.0}$ in polyblend with PANI(DBSA)$_{0.5}$. After being heated up to 450°C, the compatibility in the polyblend system was also proved when the polyblend of 50/50 showed a higher residue weight than the rest.

The shortening of the conjugation length of PANI (DBSA)$_{0.5}$ from neat HDBSA or AF(DBSA)$_{1.0}$ can be characterized by the blue shift of λ_{max} of the UV–vis spectra of PANI(DBSA)$_{0.5}$.[22] However, red shifts were seen and the secondary doping effect was recovered either for less than 50% of AF(DBSA)$_{0.5}$(HCl)$_{0.5}$ was mixed with PANI(DBSA)$_{0.5}$ or for the blended samples of PANI(DBSA)$_{0.5}$/AF(DBSA)$_{1.0}$ at high temperatures. The shielding effect of complexed DBSA on AF(DBSA)$_{0.5}$(HCl)$_{0.5}$ did not occur when less than 50% of it is present in the polyblend. The λ_{max} (at around 780 nm) of 10/90 PANI(DBSA)$_{0.5}$/ AF(DBSA)$_{1.0}$ at room temperature was red-shifted with temperature to a wavelength even higher than that of neat PANI(DBSA)$_{0.5}$. The λ_{max} in the near-IR range (>900 nm) was found with the formation of a free localized polaron band can even be seen at temperature over 220°C.

IR spectra revealed an interaction between PANI (DBSA)$_{0.5}$ and AF(DBSA)$_{1.0}$ come from the alkyl affinity and the recovery of the secondary doping effect at high temperatures involved the release of the —C—NH— group of PANI(DBSA)$_{0.5}$.

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