

# Concurrent *N*-Alkylation and Doping of Polyaniline by Alkyl Halides

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Received January 20, 2000. Revised Manuscript Received April 10, 2000

The *N*-alkylation of polyaniline (PANi) was investigated by treating the fully reduced state (leucoemeraldine or LM) and the 50% oxidized state (emeraldine or EM) directly with various alkyl halides. The degree of alkylation of LM is low (<10%), while that of EM base is much higher (can be >30%), suggesting that the imine nitrogen is more reactive as a nucleophile than the amine nitrogen in the alkylation reaction. Evidence of concurrent doping of PANi during the *N*-alkylation process was obtained using UV–visible absorption spectroscopy, FTIR spectroscopy, XPS, and conductivity measurement. The electrical conductivity of the *N*-alkylated PANi is strongly dependent on the degree of alkylation. The effects of the various alkyl halides, solvents, and reaction temperatures on the degree of alkylation and reaction rate were studied. The mechanism of the *N*-alkylation reaction and the structure of the resulting product were postulated.

## Introduction

The aniline family of polymers is basically poly(*p*-phenyleneimineamine)s in which the oxidation state can be varied from the fully reduced, leucoemeraldine (LM) to the fully oxidized pernigraniline (PNA).<sup>1–4</sup> The 50% intrinsically oxidized form or emeraldine (EM) contains alternating amine and imine repeat units.<sup>5</sup> Polyaniline (PANi) can be doped by two different ways: protonic acid doping of imine units and oxidative doping of amine units.<sup>6,7</sup> The polyanilines, either protonated or nonprotonated, are insoluble in most common organic solvents, due to the stiffness of polymer backbone and the strong hydrogen bonding between the adjacent polymeric chains. Various methods have been proposed to induce processability of PANi to enhance its potential for practical application. One way is by using organic acids, such as toluenesulfonic acid (TSA),<sup>8</sup> dodecylbenzenesulfonic acid

(DBSA), and sulfosalicylic acid (SSA),<sup>9</sup> for protonating EM. Another way is the preparation of ring or *N*-substituted polyaniline directly from the polymerization of the corresponding aniline monomers.<sup>10–14</sup> However, the substituted PANi usually has a lower conductivity ( $10^{-1}$  to  $10^{-7}$  S/cm), and lower molecular weight ( $10^3$  to  $10^4$ ), and therefore poor mechanical strength.

The replacement of the *N*-hydrogen of PANi base through acylation and alkylation has also been proven to be a practical way to prepare soluble PANi by interrupting the hydrogen bonding. For *N*-acylation of PANi, Oka et al.<sup>15</sup> used various reactive electrophilic acylating agents (e.g., acid chlorides, isocyanates), to react with the LM in *N*-methyl-2-pyrrolidone (NMP). These *N*-acyl polyanilines are less conductive than the parent PANi due to the depleted electron density on the polymeric chains by the electron-withdrawing effect of the acyl groups. As for the *N*-alkylation of PANi, Levon et al.<sup>16</sup> incorporated aliphatic alkyl chain into the LM form, while Mikhael et al.<sup>17</sup> and Chen et al.<sup>18</sup> investi-

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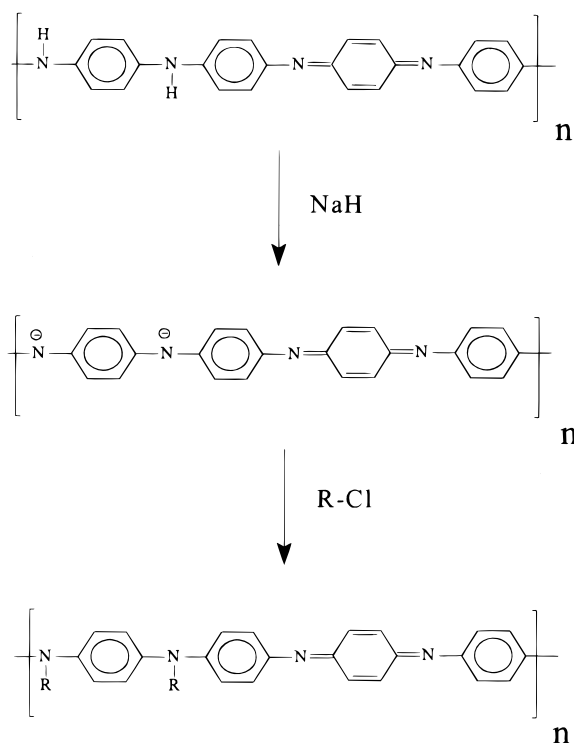
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Scheme 1



gated the modification of EM base by electrophilic substitution of the *N*-hydrogen atoms. Different kinds of alkylation agents have been used and different techniques were developed. To our knowledge, all the previous studies on alkylation to enhance solubility of the PANi have been directed at the amine nitrogen as shown in Scheme 1.

However, the reaction of emeraldine base with dimethyl sulfate can be considered to be a special way to prepare *N*-alkylated PANi.<sup>19</sup> The reaction occurs on the imine nitrogen to give a pseudo-protonated EM salt ( $[-C_6H_6-NH-C_6H_6-NH-C_6H_6-N^+(CH_3)(CH_3SO_4^-)=C_6H_4=N^+(CH_3)(CH_3SO_4^-)]_n$ ), which has an electrical conductivity of  $10^{-2}$  S/cm.

In this paper we report our studies of *N*-alkylation of PANi, with concurrent doping of the polymer. The technique employed is quite different from the method of alkylation of PANi reported in the literature where sodium hydride (NaH) was used to improve the reactivity of amine nitrogen. The effects of the various alkyl halides, solvents, temperatures, and oxidation states of the PANi on the alkylation reaction were studied. The resulting product was characterized using FTIR spectroscopy, UV-visible absorption spectroscopy, and X-ray photoelectron spectroscopy (XPS). Conductivity and elemental composition of the *N*-alkylated PANi were also determined. From these analyses, postulates were made regarding the mechanism and product structure.

## Experimental Section

**Preparation of Polyaniline (Powder, Film, and Coating on LDPE film).** Polyaniline was synthesized via the oxidative polymerization of aniline with ammonium persulfate

in 0.5 M  $H_2SO_4$  according to the method described in the literature for 1 M HCl.<sup>20</sup> It was converted to EM base by treatment with excess 0.5 M NaOH for 24 h, followed by washing with deionized water until the filtrate was neutral. The base powder was dried under reduced pressure for 24 h. Free-standing emeraldine base (EM base) film of about 10–20  $\mu$ m in thickness was prepared by casting from *N*-methyl-2-pyrrolidinone (NMP) solution containing 5 wt % of EM base. In the preparation of PANi coating on low-density polyethylene (LDPE) film, the LDPE film (obtained from Goodfellow Ltd. of Cambridge, UK) of 0.125 mm in thickness and 15 mm  $\times$  15 mm in area was first pretreated with  $O_2$  plasma for 60 s, and then immersed in the above-mentioned polymerizing solution of aniline for 2 h. The film was then dried under reduced pressure for 2 h. The EM base coating on LDPE film was prepared by deprotonating the as-synthesized PANi coating in 0.5 M NaOH solution for 2 h, followed by rinsing with deionized water.

***N*-Alkylation.** Four alkyl bromides, 2-bromo-2-methylbutane ( $C_5H_{11}Br$ ), 1-bromoheptane ( $C_7H_{15}Br$ ), 1-bromododecane ( $C_{10}H_{21}Br$ ) (Aldrich), 1-bromododecane ( $C_{12}H_{25}Br$ ) (Fluka), as well as benzyl chloride (BDH) and 1-iodobutane (Fluka) were used. The alkyl halide was diluted in a solvent to a volume concentration of 10%. The solvents used were dimethylformamide (DMF) (Baker) and isopropanol (2-propanol) (Merck). The solution was heated in a water bath at constant temperature. Polyaniline powder, film, or coating on LDPE was treated in the solution for a period of time and then taken out, washed with excess 2-propanol and acetone to remove the unreacted alkyl halide and solvent completely. The sample was dried under reduced pressure before being subjected to further characterization.

**Sample Characterization.** PANi powders before and after alkylation were mixed with KBr to make the test pellet specimens for FTIR analysis using a BIO-RAD FTS 135 spectrophotometer. Changes in the UV-visible absorption spectra of EM coating on LDPE film after alkylation were monitored on a UV-vis-NIR scanning spectrophotometer (Shimadzu UV-3101 PC), using the pristine LDPE film as the reference. The bulk chemical composition was analyzed using a Perkin-Elmer model 2400 CHN elemental analyzer. The total bulk Br content was determined by the Schöniger combustion method in which the chemical titration was carried out using mercuric(II) nitrate.<sup>21</sup>

The surface compositions were measured using X-ray photoelectron spectroscopy (XPS) on a VG ESCALAB Mk II spectrometer with the Mg  $K\alpha$  X-ray source (1253.6 eV photons). The X-ray source was run at a reduced powder of 120 W (12 kV and 10 mA). The core-level spectra were obtained at a photoelectron takeoff angle ( $\alpha$ , with respect to sample surface) of 75°. The pressure in the analysis chamber was maintained at  $10^{-8}$  mbar or lower during the measurements. To compensate for surface charging effects, all binding energies were referenced to the C 1s neutral carbon peak at 284.6 eV. In spectral deconvolution, the full width at half-maximum of the peak components in a spectrum was kept constant. Surface chemical compositions were determined from peak area ratios corrected with the appropriate experimentally determined sensitivity factors, and were accurate to  $\pm 10\%$ .<sup>22</sup>

The two-probe technique was used to measure the sheet resistance ( $R_s$  in  $\Omega$ /sq) of the film (conductivity =  $1/(R_s \times \text{thickness of the film})$ ).<sup>23</sup> A comparison of the conductivities calculated from the sheet resistances of a number of films and the conductivities of the corresponding films as measured by the four-probe technique was carried out. For the more

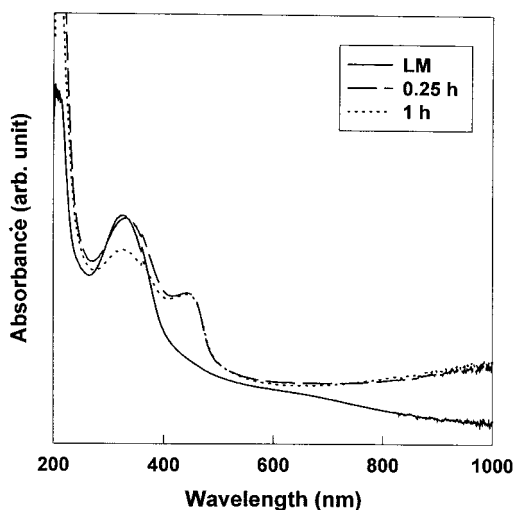
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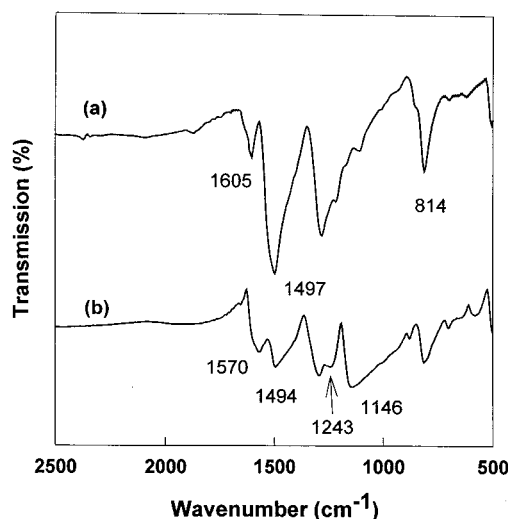


**Figure 1.** UV-visible absorption spectra of LM coating on LDPE before and after treatment with 10 vol %  $C_5H_{11}Br$  in 2-propanol at 80 °C.

conductive films ( $R_s \approx 10^3 \Omega/sq$ ), the two values are generally within a factor of 2, while for the more highly insulating films ( $R_s \approx 10^{10} \Omega/sq$ ), the two values are of the same order of magnitude. The  $R_s$  measurements are more easily carried out than the four-probe conductivity measurements and were used throughout this work to provide the means for comparing the surface conductivity changes of the films under various experimental conditions.

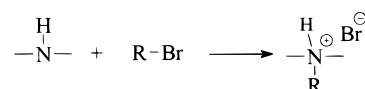
## Results and Discussion

**1. N-Alkylation of Leucoemeraldine (LM).** As the LM coating on LDPE film was treated with 10 vol %  $C_5H_{11}Br$  in 2-propanol ( $\sim 0.78 M$ ) at 80 °C, the film showed a color change from colorless to green, concurrent with a sharp decrease of sheet resistance ( $R_s$ ) from  $10^{10}$  to  $10^6 \Omega/sq$ . The UV-visible absorption spectrum of freshly prepared LM (Figure 1) reveals a strong absorption band at 325 nm, which is assigned to the  $\pi-\pi^*$  transition of the polymer chain.<sup>24-26</sup> An insignificant absorption at 635 nm, attributed to a charge-transfer exciton-like transition from the highest occupied energy level to the lowest unoccupied energy level,<sup>24,25</sup> indicates a very small fraction of quinoid (Q) groups present in the thin coating layer. A new absorption band at 441 nm was found after treatment for 0.25 h, while the absorption band at 345 nm diminished significantly after 1 h of the alkyl bromide treatment. The same changes in the UV-visible spectra were found when the solution was degassed with argon before the immersion of the LM coating. The polaron band for PANi at 441 nm<sup>24,27,28</sup> suggests that the some LM units have been doped during the treatment, due to the alkylation of the amine nitrogen via a nucleophilic substitution as shown in Scheme 2.



**Figure 2.** FTIR spectra of LM powder (a) before and (b) after treatment with 10 vol %  $C_5H_{11}Br$  in 2-propanol at 80 °C for 4 h.

### Scheme 2



The concurrent effect of doping and alkylation of LM powder can also be seen from the FTIR spectroscopic analysis. The FTIR transmission spectra of LM powder before and after treatment with  $C_5H_{11}Br$  in 2-propanol at 80 °C for 4 h are compared in Figure 2. It was found that the powder changed color from gray to dark green after the treatment. The spectrum of pristine LM powder exhibits a very low intensity ratio of the 1605 and 1497  $cm^{-1}$  peaks, which are associated with the aromatic ring stretching (quinoid (Q) ring and benzoid (B) ring, respectively).<sup>4,29</sup> The spectrum of LM powder after treatment showed an increase in intensity and significant broadening of the 1146  $cm^{-1}$  peak, which implies some degree of electron delocalization and an increase in electrical conductivity.<sup>4,29,30</sup> The red-shift (from 1605 to 1570  $cm^{-1}$ ) of the Q ring peak is also the characteristic of doped PANi.<sup>28,31</sup> The presence of the absorption peak at 1243  $cm^{-1}$ , attributed to the aliphatic carbon-nitrogen stretching,<sup>32</sup> suggests that the alkyl substituents are linked on the nitrogen of the polymer chain.

The elemental analysis of LM powder after treatment in 10 vol %  $C_5H_{11}Br$  in 2-propanol at 80 °C for 4 h (LM- $C_5H_{11}Br$ ) indicates that the degree of alkylation of LM powder is only 8% (Table 1), which suggests that the reactivity of amine nitrogen is low. In contrast, in a previous study, LM was pretreated with sodium methylsulfinyl carbanion before the alkylation reaction, and under such condition, the degree of alkylation is substantially higher.<sup>16-18</sup>

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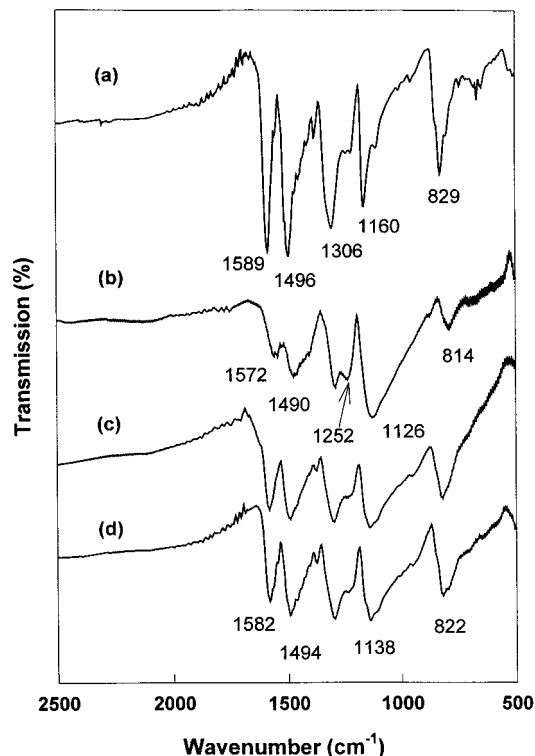
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**Table 1. Elemental Analyses of LM and EM Powders before and after Treatment with Alkyl Bromides**

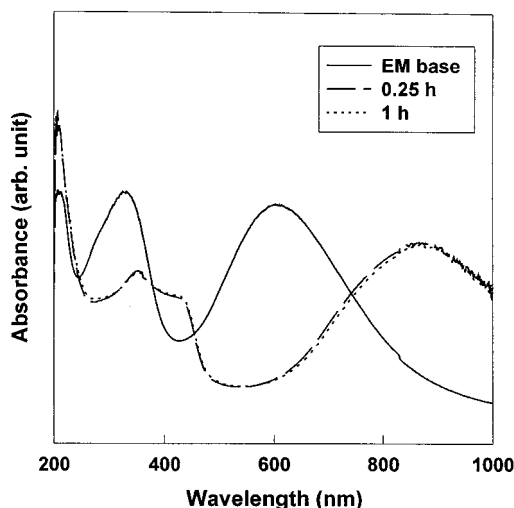
sample name <sup>a</sup>	elemental content (wt%)				degree of alkylation <sup>b</sup>
	C	H	N	Br	
LM	75.43	5.49	15.40		
LM-C <sub>5</sub> H <sub>11</sub> Br	71.93	4.92	13.65	3.63	0.08
EM	74.42	4.67	12.06		
EM-C <sub>5</sub> H <sub>11</sub> Br	57.30	5.59	10.43	17.83	0.31
EM-C <sub>7</sub> H <sub>15</sub> Br	71.21	5.51	11.61	4.83	0.17
EM-C <sub>10</sub> H <sub>21</sub> Br	72.08	5.42	12.10	4.47	0.12

<sup>a</sup> Samples were treated in 10 vol % solution of R-Br in 2-propanol at 80 °C for 4 h. <sup>b</sup> Degree of alkylation is defined as the percentage of the alkylated N and calculated from the N content.



**Figure 3.** FTIR spectra of EM base powders (a) before and after treatment with 10 vol % (b) C<sub>5</sub>H<sub>11</sub>Br, (c) C<sub>7</sub>H<sub>15</sub>Br, or (d) C<sub>10</sub>H<sub>21</sub>Br in 2-propanol at 80 °C for 4 h.

**2. N-Alkylation of Emeraldine (EM).** Evidence of N-Alkylation and Doping. When EM base powder was treated with C<sub>5</sub>H<sub>11</sub>Br in 2-propanol at 80 °C for 4 h, the color of the powder changed from dark brown to dark green. The FTIR spectra of EM base powder before and after such treatment are compared in parts a and b of Figure 3. The absorption bands at 1496 and 1589 cm<sup>-1</sup> for pristine EM base (Figure 3a) have been associated with the aromatic ring stretching modes for benzenoid (B) ring and quionoid (Q) ring, respectively. The Q/B absorption intensity ratio is slightly less than unity. After the alkylation reaction, the spectrum of EM powder shows an increase in intensity and broadening of the 1126 cm<sup>-1</sup> (shifted from 1160 cm<sup>-1</sup>) peak, similar to the changes observed in the spectrum of treated LM (Figure 2b). The decrease in intensity and red-shifting of the 1589 and 1496 cm<sup>-1</sup> peaks in Figure 3b are characteristics of EM salt.<sup>28,31,33,34</sup> The presence of the



**Figure 4.** UV-visible absorption spectra of EM base coating on LDPE before and after treatment with 10 vol % C<sub>5</sub>H<sub>11</sub>Br in 2-propanol at 80 °C.

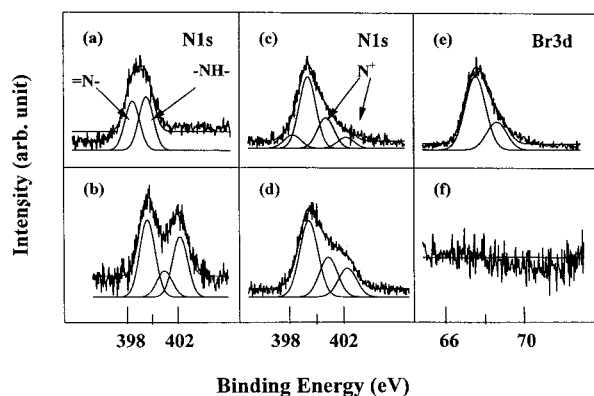
absorption peak at 1252 cm<sup>-1</sup> attributed to the aliphatic C-N stretching suggests that the alkyl substituents are linked on the nitrogen of the polymer chain, while neither the position nor the intensity of the aromatic C-N stretching band at 1306 cm<sup>-1</sup> changes after alkylation. The presence of the absorption band at 830 cm<sup>-1</sup>, characteristic of the C-H out-of-plane bending vibration of the 1,4-disubstituted benzene ring, together with the absence of a splitting of this peak into two peaks at 800 and 870 cm<sup>-1</sup>, indicates that no ring substitution occurred in the alkylation reaction.<sup>18,29</sup>

The conversion of EM from the base to the conducting form upon alkylation can also be readily seen from the UV-visible absorption spectra of an EM base coating on LDPE recorded during the alkylation treatment. Figure 4 shows the progression of the reaction in which an EM base coating on LDPE was alkylated by treatment with C<sub>5</sub>H<sub>11</sub>Br. Within a short period of time from the start of the reaction, the exciton-like transition band at 610 nm disappears and the intensity of the  $\pi-\pi^*$  transition at 330 nm is much reduced, while two new bands at 435 and 800–900 nm appear. The band at 800–900 nm is attributed to the intraband free carrier excitations and the absorption band at 435 nm is assigned to the polaron transitions. These bands together with the greatly diminished  $\pi-\pi^*$  transition band are present only in protonated and conductive PANi and are usually attributed to the conversion of unprotonated quinoid imine structure to the protonated form (polaron structure).<sup>24–34</sup> The spectra in Figure 4 also show that the alkylation of EM coating on LDPE proceeds so rapidly that no further reaction occurs after 0.25 h. This is partially because the PANi coating layer is very thin.

The N 1s XPS core-level spectra of free-standing EM base film before and after treatment with HClO<sub>4</sub> and C<sub>5</sub>H<sub>11</sub>Br are compared in Figure 5. Comparing the spectra of the EM film before and after protonated with HClO<sub>4</sub> (Figure 5, parts a and b, respectively), it is clear that upon protonation the imine ( $-N=$ ) peak (at 398.2 eV) has completely disappeared and a high BE tail

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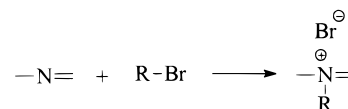
**Figure 5.** XPS spectra of EM films: (a) EM base; (b) EM base treated with 1 M HClO<sub>4</sub> (EM-HClO<sub>4</sub>); (c) EM base treated with 10 vol % C<sub>5</sub>H<sub>11</sub>Br in 2-propanol at 80 °C for 4 h; (d) EM-HClO<sub>4</sub> treated using the same condition as c; (e) same as c; and (f) same as d.

**Table 2. Surface Compositions from XPS of EM Base Films Treated with R-Br (10 vol % in 2-Propanol, 80 °C, 4 h)**

sample name	=N-/N	-NH-/N	N <sup>+</sup> /N	Br <sup>-</sup> /N
EM	0.45	0.55		
EM-C <sub>5</sub> H <sub>11</sub> Br	0.06	0.56	0.38	0.36
EM-C <sub>7</sub> H <sub>15</sub> Br	0.17	0.59	0.24	0.21
EM-C <sub>10</sub> H <sub>21</sub> Br	0.22	0.58	0.20	0.17

attributed to the formation of positively charged nitrogen (N<sup>+</sup>)<sup>4,35</sup> becomes a dominant feature. The N 1s spectrum of EM base film after treatment with C<sub>5</sub>H<sub>11</sub>Br also shows a decrease in the proportion of imine units and an increase in the proportion of N<sup>+</sup> after the alkylation (Figure 5c), while the amine (-NH-) content remains approximately constant (Table 2). This result implies that the alkylation occurs mainly on the nitrogen of the imine units instead of the amine units of EM under the selected reaction conditions. In other words, most of the N<sup>+</sup> produced in the alkylation treatment is from the conversion of imine nitrogen, similar to the protonation of EM by acids. The Br 3d spectrum of the alkylated EM (Figure 5e) reveals the existence of Br<sup>-</sup> at about 67.5 eV,<sup>36</sup> with no other bromide species present. These Br<sup>-</sup> anions serve as the counterions of N<sup>+</sup>, and the Br<sup>-</sup>/N ratio is quite close to the N<sup>+</sup>/N ratio (Table 2), which is expected if charge neutrality is to be maintained. An experiment was carried out in which HClO<sub>4</sub>-protonated EM film was subjected to the same alkylation conditions. A comparison of the N 1s core-level spectrum of this sample (Figure 5d) with Figure 5c shows a change in line shape which is ascribed to a small amount of deprotonation by the solvent. No bromide ions were found in this sample (Figure 5f). This result suggests that protonated EM cannot be alkylated under the selected conditions, because the imine groups after protonation with protonic acid lose the nucleophilic activity. Because of the continuous delocalization of the conjugated  $\pi$ -system along the PANi molecular chain by resonance, it can be expected that there is loss of the nucleophilic activity of the remaining unalkylated units. Hence, the reactivity of EM will decrease with

**Scheme 3**



the increasing degree of alkylation, leading a decrease in reaction rate.

The elemental analysis results of EM powder before and after treatment with C<sub>5</sub>H<sub>11</sub>Br are listed in Table 1. The degree of alkylation of EM powders by C<sub>5</sub>H<sub>11</sub>Br is 31%, much higher than that of LM, further confirming the greater ease of alkylation of the imine nitrogen of PANi. The alkylation of the imine unit would proceed as shown in Scheme 3.

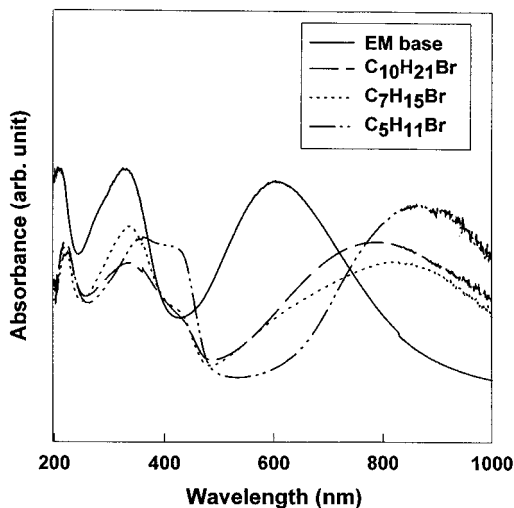
The alkylation on the nitrogen of PANi should be classified as aliphatic nucleophilic substitution, in which nitrogen with an electron pair forming the new band serves as the attacking reagent (the nucleophile), and the bromide ion coming away with an electron pair serves as the leaving group (the nucleofuge).<sup>37</sup> Due to the electron delocalization along the PANi molecular chain by resonance, it is difficult to identify whether the two aliphatic groups are on adjacent nitrogen atoms. The alkylation not only produces *N*-substituted polyaniline, but the polymer is also doped at the same time with Br<sup>-</sup> anions serving as counterions to the N<sup>+</sup> produced as shown in Scheme 3. Since no protonic acid is employed and the number of electrons in the PANi chain remains unchanged in the treatment process, the alkylation of nitrogen can be considered as another method for doping of PANi, besides the recognized protonation and the redox method.

**Effect of Different Alkyl Halides.** In Figure 3, the FTIR spectra of EM powder after alkylation treatment with C<sub>7</sub>H<sub>15</sub>Br and C<sub>10</sub>H<sub>21</sub>Br (Figures 3c and 3d, respectively) are compared with that obtained after alkylation with C<sub>5</sub>H<sub>11</sub>Br under the same conditions (Figure 3b). The features described earlier for Figure 3b are also observed in parts c and d of Figure 3. However, the changes observed in the latter two spectra are not as prominent as the former. The result implies that the longer chain alkyl halides may not be as effective in the alkylation reaction. The UV-visible absorption spectra of EM coating on LDPE film after alkylation with these three different alkyl bromides under the same conditions are compared in Figure 6. The C<sub>5</sub>H<sub>11</sub>Br-treated sample has a much reduced band in the 330 nm region, a higher intensity absorption band at 435 nm coupled with an absorption band in the 800–900 nm region which is of higher intensity and red-shifted to a greater extent than what was observed in the spectra of the other two samples. These features are consistent with the more highly doped PANi. The differences between the spectra of the EM coating treated with C<sub>7</sub>H<sub>15</sub>Br and C<sub>10</sub>H<sub>21</sub>Br are not very substantial, indicating that the increase of aliphatic chain length by three carbons beyond C<sub>7</sub>H<sub>15</sub>Br does not have a dramatic effect on the reaction. The same conclusion was obtained when other alkyl bromides such as 1-bromododecane and 3-bromomethylheptane were used.

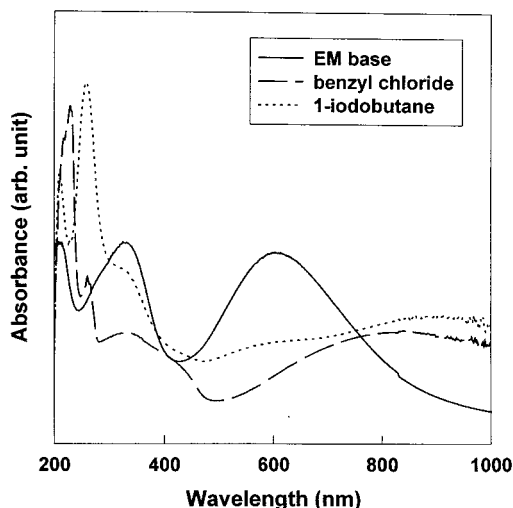
(35) Kang, E. T.; Neoh, K. G.; Tan, K. L. *Adv. Polym. Sci.* **1993**, *106*, 157.

(36) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. *Handbook of X-ray Photoelectron Spectroscopy*; Chastain, J., Ed.; Perkin-Elmer Corporation: Eden Prairie, MN, 1992; p 98.

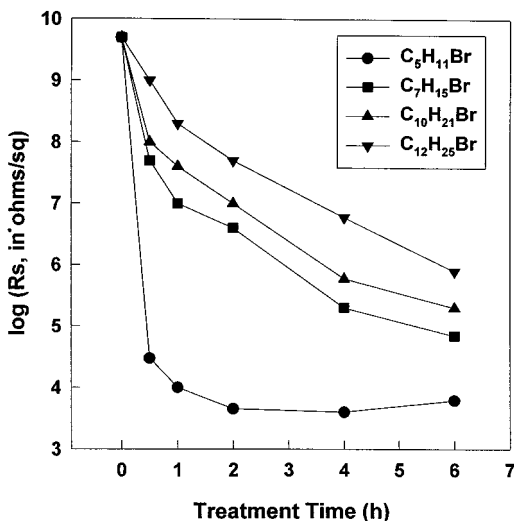
(37) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; pp 359–500.



**Figure 6.** UV-visible absorption spectra of EM base coating on LDPE before and after treatment with 10 vol % alkyl bromides in 2-propanol at 80 °C for 2 h.



**Figure 8.** UV-visible absorption spectra of EM base coating on LDPE before and after treatment with 10 vol % benzyl chloride and 1-iodobutane in 2-propanol at 80 °C for 1 h.



**Figure 7.** Sheet resistance ( $R_s$ ) of EM base films treated with 10 vol % alkyl bromides in 2-propanol at 80 °C.

The inferences from the FTIR and UV-visible absorption spectroscopy analyses regarding the decrease in the extent of doping with the use of longer chain alkyl halides are supported by the low bromide content and degree of alkylation when such halides are used, as shown in Table 1. It can be expected that the electrical conductivity of the various alkylated PANi would be highly dependent on the degree of alkylation. This is illustrated by Figure 7. The reaction of  $C_5H_{11}Br$  with EM base free-standing film is rapid and after 2 h the asymptotic sheet resistance of  $5 \times 10^3 \Omega/sq$  has been achieved. This value compares favorably with the resistance of  $\sim 10^3 \Omega/sq$  obtained when EM film is treated with 1 M  $HClO_4$ .<sup>38</sup> In contrast, for the other three longer chain alkyl bromides, the reaction rate is much reduced and after 6 h, the resistance has not reached an asymptotic value, implying that the reaction is still continuing. The significantly higher alkylation rate and degree of alkylation obtained with  $C_5H_{11}Br$  is due to the much more stable tertiary carbonium ion,

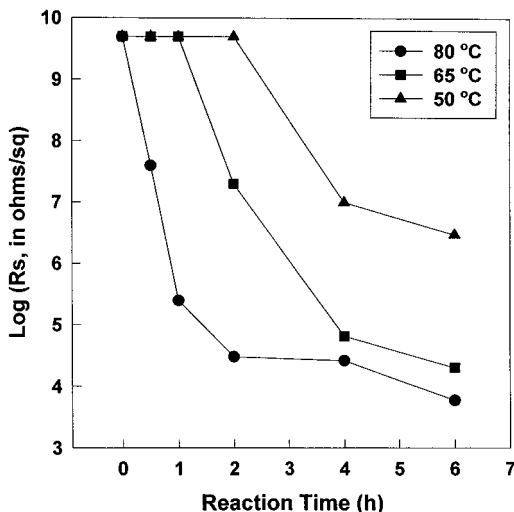
supporting the postulate that the alkylation follow the substitutional nucleophilic unimolecular ( $S_N1$ ) mechanism.<sup>37,39</sup> The steric effect of the longer chain alkyl group may also contribute to the difference observed. Although the same volume concentration of alkyl halides (10 vol %) was used in all these experiments, which means that the longer chain alkyl halides would have a lower molar concentration, the difference in the molar concentration was found not to have a significant effect on the reaction rate and degree of alkylation (as deduced from sheet resistance measurement).

So far, the discussions have centered on the use of alkyl bromides for converting PANi to a doped state. Experiments using benzyl chloride and 1-iodobutane were also carried out and the results show that similar concurrent doping and *N*-alkylation of PANi can be achieved (Figure 8). It has been reported earlier<sup>17</sup> that benzyl chloride is not effective in the *N*-alkylation of EM base, but our results in Figure 8 show that the spectrum of EM base coating after treatment with 10 vol % benzyl chloride in 2-propanol at 80 °C for 1 h is characteristic of doped EM, and the EM base free-standing film after such treatment has a  $R_s$  of  $10^5 \Omega/sq$  compared to  $> 10^9 \Omega/sq$  for EM base.

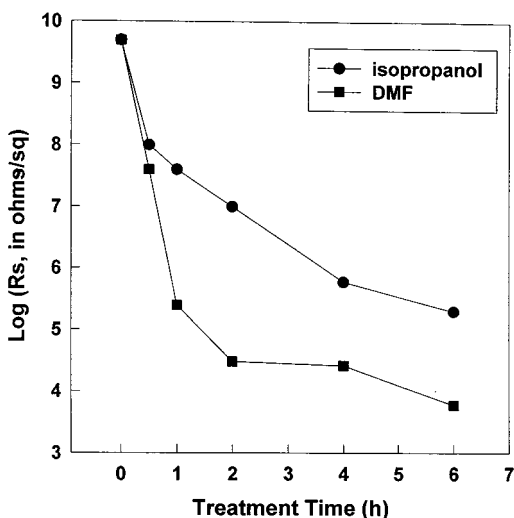
**Effect of Different Reaction Conditions.** It was observed that when the reaction temperature is not substantially higher than room temperature, there is an initial lag period where there is no change in the sheet resistance of the EM base film upon treatment with the alkyl bromide. For example, in the case of EM base film treated with 10 vol %  $C_{10}H_{21}Br$  in DMF at 50 °C,  $R_s$  was unchanged for 2 h. The alkylation reaction is accelerated by an increase in the reaction temperature as shown by the shorter lag period and the lower  $R_s$  achieved at the higher temperature keeping reaction time constant (Figure 9). An adequately high temperature is necessary to achieve a fast reaction rate and/or a high degree of alkylation. However, because of the different reactivities of the different alkyl halides, the effect of temperature will be different for each alkyl

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**Figure 9.** Sheet resistance ( $R_s$ ) of EM base films treated with 10 vol %  $C_{10}H_{21}Br$  in DMF at different temperatures.



**Figure 10.** Sheet resistance ( $R_s$ ) of EM base films treated with 10 vol %  $C_{10}H_{21}Br$  in DMF and 2-propanol at 80 °C.

halide. The reaction temperature is limited by the vapor pressure of the solvent but the solvent itself also has a strong effect on the alkylation reaction. The more polar solvent can result in a faster reaction, since polar

solvent reduces the energy of an ionic transition state in the first step of the  $S_N1$  reaction. From Figure 10, it can be seen that the  $R_s$  of the  $C_{10}H_{21}Br$ -treated sample in DMF is substantially lower than the corresponding sample with 2-propanol as solvent. The  $R_s$  of the  $C_{10}H_{21}Br$ -treated sample in DMF after 6 h treatment is nearly 2 orders of magnitude lower than that of the corresponding sample treated in 2-propanol (Figure 10) and the former value is comparable to that of the  $C_5H_{11}Br$ -treated sample in 2-propanol for 1 h (Figure 7). The fact that DMF is an aprotic solvent while 2-propanol is a protic solvent may also contribute to the difference in reaction rates.<sup>37,39</sup> Although PANi base is somewhat soluble in DMF, the solubility of the *N*-alkylated PANi is quite limited. After treatment with water or dilute base solution to remove the halide counterions, the *N*-alkylated PANi exhibits a high degree of solubility in various organic solvents.

### Conclusion

The *N*-alkylation of PANi was achieved by treatment of LM or EM base with various alkyl halides. The degree of alkylation of LM is low (<10%), while that of EM base is much higher (can be >30%), suggesting that the imine nitrogen is more reactive as a nucleophile than the amine nitrogen in the reaction. The concurrent conversion of PANi from an insulating state to the conducting state as a result of *N*-alkylation by alkyl halides was evident from UV-visible absorption spectroscopy, FTIR, XPS, and conductivity measurement. The electrical conductivity of the *N*-alkylated PANi is strongly dependent on the degree of alkylation, with a higher conductivity being obtained for the PANi with a higher degree of alkylation.

The *N*-alkylation reaction follows the aliphatic nucleophilic substitution mechanism. Both the degree of alkylation and reaction rate are affected by the structure of the alkyl halides, solvents, and reaction temperature. 2-bromo-2-methylbutane ( $C_5H_{11}Br$ ) exhibits high reactivity both in protic solvent and aprotic solvents, while the longer straight chain alkyl halide has a lower reactivity. For the latter, a high temperature is necessary for the alkylation to proceed.

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