## Preparation and Characterization of Poly(2-chloroaniline)/ SiO<sub>2</sub> Nanocomposite via Oxidative Polymerization: Comparative UV–Vis Studies into Different Solvents of Poly(2-chloroaniline) and Poly(2-chloroaniline)/SiO<sub>2</sub>

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Received 21 July 2005; revised 28 January 2006; accepted 17 February 2006 DOI 10.1002/app.24266 Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Poly(2-chloroaniline)/silica (P2ClAn)/SiO<sub>2</sub> nanocomposites have been chemically prepared by oxidative polymerization of 2-chloroaniline in acidic medium containing SiO<sub>2</sub>. The prepared composites were characterized by FTIR, UV–vis, TGA, XRD, SEM, ESEM, conductivity, and magnetic susceptibility. The incorporation of P2ClAn in composites was endorsed by FTIR studies. The effect of the solution concentration of P2ClAn and P2ClAn/SiO<sub>2</sub> prepared in protonated, deprotonated, and reprotonated structures on the UV–vis spectra was investigated into three different solvents (DMF, NMP, and H<sub>2</sub>SO<sub>4</sub>). In all forms, the oxidation state of P2ClAn and P2ClAn/SiO<sub>2</sub> composite increased with increasing concentration of the testing solution into H<sub>2</sub>SO<sub>4</sub>. Thermogravimetric study exhibited that the composite has a higher thermal stability than P2ClAn. XRD measurement of

#### INTRODUCTION

Electrically conducting polymers are novel class of synthetic metals that combine the chemical and mechanical properties of polymers with the electronic properties of metals and semiconductors.<sup>1</sup> Polyaniline (PAni) is one of the most intensively conducting polymers studied during the last decade. It is highly conducting, easy to synthesize both chemically as a green powder or electrochemically as a film.<sup>2–4</sup> The chemical method has a great importance since it is very feasible route for the mass production of PAni.

Composites of conjugated polymers are interesting because of their potential for combining properties that are difficult to attain separately with individual components. Nanocomposites based on conducting polymer and transition metal oxides have been intensively investigated during recent years due to their potential applications as electrode material in lithium batteries.<sup>5</sup> These composites were prepared by polymerization of the monomers in the presence of disthe composite revealed that the crystal structure of incorporated SiO<sub>2</sub> undergone a distortion and converted into amorphous. Thus, the XRD pattern of P2ClAn was predominant. SEM analysis results revealed interesting morphological features for the composites converted to different forms and confirmed the formation of monodispersed composite particles. ESEM image of P2ClAn/SiO<sub>2</sub> has particle diameter of less than 1  $\mu$ m. The conductivity of P2ClAn and P2ClAn/SiO<sub>2</sub> was measured by four-probe technique. Magnetic susceptibility measurements revealed that the composite has a paramagnetic properties. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 935–943, 2006

**Key words:** conducting polymer; morphology; UV-visible spectroscopy; poly(2-chloroaniline); SiO<sub>2</sub>

persed oxide. Three methods for deriving such nanocomposites are known.<sup>6</sup> The first one includes the intercalation of the monomers into the host matrix followed by their polymerization due to the presence of an external oxidizing agent. In the second method, the redox properties of the host (metal oxide) ensure *in situ* polymerization as well as intercalation of polymer macromolecules inside the host particles. Several inorganic nanoparticles such as CdS and CuS,<sup>7</sup> clay,<sup>8</sup> maghemite,<sup>9</sup> MnO<sub>2</sub>,<sup>10</sup> TiO<sub>2</sub>,<sup>11</sup> and ZrO<sub>2</sub><sup>12</sup> had been used for the conductive PAni nanocomposites.

It is well known that PAni has a very strong pH sensitivity, which is deprotonated on a reversible acid-deprotonated reaction between the half-oxidized emeraldine deprotonated (EB) and the emeraldine salt (ES) form of PAni. The emeraldine deprotonated form of PAni and its derivatives can be protonated with a sufficiently strong acid due to the presence of basic sites (amine and imin groups) in the polymer structure.<sup>13</sup> Among polyaniline's derivations, poly (2-chloroaniline) (P2ClAn) shows better solubility and processibility but it has lower conductivity than that of PAni. The emeraldine salt (ES; protonated form of EB) is, however, the only electrically conducting form of the protonated forms of P2ClAn (Scheme 1).

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Journal of Applied Polymer Science, Vol. 102, 935–943 (2006) © 2006 Wiley Periodicals, Inc.



Poly (2-c hloroa niline) b ase

**Scheme 1** The protonated emeraldine form of poly (2-chloroaniline) (one of the possible chemical representations) converts to poly(2-chloroaniline) deprotonated after the deprotonation in the alkaline media; e.g., in ammonium hydroxide solutions. A<sup>-</sup> represents an arbitrary anion, e.g., chloride.

UV–vis spectroscopy is one of the mostly adopted techniques in characterizing the structures of PAni and its derivatives,<sup>14</sup> for its convenience<sup>15</sup> as compared with X-ray photoelectron spectroscopy,<sup>16</sup> etc. The UV–vis spectrum of PAni, which is one of the most studied conducting polymers, in deprotonated form is dominated by two absorption peaks at ~320 nm (Band I) and ~610 nm (Band II), respectively. Band I often assigned to  $\pi \rightarrow \pi^*$  transition in benzenoid structure.<sup>17</sup> The absorption in the visible range, i.e., Band II, is ascribed to excision formation in the quinonoid rings.<sup>18</sup>

The intensity ratio of Band II to Band I ( $I_2/I_1$ ) indicates the relative amount of quinoid diimine unit in PAni molecules, viz the oxidation state of PAni,<sup>19,20</sup> which plays a key role in determining the property of PAni. To date, UV–vis spectroscopy is still being used by many researchers in characterizing the oxidation state of PAni.<sup>21,22</sup>

Incorporation of inorganic nanoclusters into polymer matrices can dramatically improve their processability.<sup>7,23,24</sup> Although there are so many candidates as the polymeric matrix, one particular interest is the integration of inorganic nanoclusters with conducting polymers because the resulting nanocomposites may possess unique electrical and optical properties. Because of these properties, such materials are expected to find applications in electrochromic devices, nonlinear optical system, and photoelectrochemical devices.

Here, we selected PClAn as polymeric matrix because it has better solubility than polyaniline.<sup>25</sup> P2ClAn/SiO<sub>2</sub> composite was synthesized using SiO<sub>2</sub> to modify properties of P2ClAn. To clarify optical properties of composite, detail UV–vis study was done using different solvents. We present the effects of the solution concentration and solvent type on UV–vis spectroscopy for both P2ClAn and P2ClAn/SiO<sub>2</sub> using their protonated, deprotonated, and reprotonated forms. P2ClAn/SiO<sub>2</sub> composite is novel and its properties were compared with that of P2ClAn. We used three different solvents, DMF,

NMP, and  $H_2SO_4$ . The preparation, characterization, and property evaluation of P2ClAn/SiO<sub>2</sub> composites are highlighted by different techniques in this article.

#### **EXPERIMENTAL**

#### Materials

2-Chloroaniline was purified by distillation at reduced pressure before use.  $SiO_2$  (silica, 99.8%, Cat No: 381268) was received from Aldrich and it has particle size of 0.007 µm. Ammonium peroxydisulfate (APS), ammonia solution, sulfuric acid, hydrochloric acid, *N*,*N*-dimethyl formamide (DMP), *N*-methylpyrrolidone, and 2-chloroaniline were purchased from Aldrich.

#### Polymerization of 2-chloroaniline

Polymerizations were carried out in a 250-mL threenecked round bottom flask equipped with magnetic stirring. Typical recipies are described as follows: 2-chloroaniline was dissolved in 1*M* HCl aqueous solution. The solution was cooled down to 5°C and a solution of APS, with  $n_{\text{monomer}}/n_{\text{oxidant}} = 2$ , was added dropwise. Polymerization was carried out under nitrogen and controlled stirring for 24 h. At the end of polymerization, poly(2-chloroaniline) was filtered and washed with 1*M* HCl solution and distilled water before to be dried overnight at 60°C under vacuum.

#### Synthesis of P2ClAn/SiO<sub>2</sub> nanocomposite

P2ClAn/SiO<sub>2</sub> nanocomposite was prepared by "*in situ*" deposition oxidative polymerization of 2-chloroaniline hydrochloride using APS as oxidant in the presence of SiO<sub>2</sub> powders cooled by an ice bath. Before adding aqueous solution of APS, the suspension of SiO<sub>2</sub> and monomer solution was mixed to obtain a homogenous dispersion. The aqueous solution of APS was slowly added dropwise with vigorous stirring. The precipitated composite powder was filtered and washed with HCl solution and distilled water till the filtrate become colorless to remove the byproduct, excess monomer, and oligomer and dried overnight at 60°C under vacuum. The amount of SiO<sub>2</sub> in nanocomposite was calculated as 20%.

The resulting P2ClAn and P2ClAn/SiO<sub>2</sub> emeraldine salts were converted into its deprotonated form (P2ClAn(EB)/SiO<sub>2</sub>) by treating with 1*M* ammonium hydroxide solution. The deprotonated form of homopolymer and its composite were thoroughly washed with distilled water, and then vacuum-dried to constant mass for use. After deprotonation process, samples were reprotonated using 1*M* HCl solution.

#### Characterization

Fourier transform infrared (FTIR) spectra were recorded between 400 and 4000 cm<sup>-1</sup> from KBr pel-

lets on a Perkin-Elmer Spectrum BX FTIR system (Beaconsfield, Buckinghamshire, HP91QA, England). The direct current electrical conductivity of the protonated P2ClAn and P2ClAn/SiO<sub>2</sub> nanocomposite was measured by standard four-probe method. UVvis spectra were recorded between 250 and 900 nm using a 1 cm path length quartz cuvette, and pure DMF, NMP, and H<sub>2</sub>SO<sub>4</sub> solvents were used as the reference on a Perkin-Elmer Lambda 20 UV-vis spectrophotometer. Five testing solutions at appropriate concentrations from 0.01 to 0.05 g/L for subsequent spectroscopic studies were prepared by dissolving 0.005 g powders in predetermined volumes of DMF, NMP, and H<sub>2</sub>SO<sub>4</sub>. For SEM analysis, samples were sputter coated with gold layers and photographs were taken on a scanning electron microscope model Jeol 5600-LV Model Scanning (Tokyo, Japan). Particle diameter analysis was done by using Philips ESEM-FEG XL30 Model (FEI Company B606L, USA) environmental scanning electron microscopy Field Emission Gun instrument operating at 10 kV at low vacuum. The sample was mounted on a doublesided Silver cohesive sheet; no gold coating is needed. Thermal stability of P2ClAn and its nanocomposites with SiO<sub>2</sub> was investigated by Perkin-Elmer model thermal parametric analyzer (Beaconsfield, Buckinghamshire, HP91QA, England) with nitrogen (a pure gas) at a flow rate of 35 mL/min. Magnetic susceptibilities were measured using Magway MSB Mk1 Model (Sherwood Scientific) Gouy Scale, according to the procedure reported elsewhere.<sup>4</sup> X-ray diffraction studies were performed by using Philips X-ray diffractometer (LabX, Midland, Canada) with CuKa as radiation source.

#### **RESULTS AND DISCUSSION**

Figures 1(a)–1(c) present the FTIR spectra of P2ClAn (protonated), P2ClAn (deprotonated), and (reprotonated) forms. The main peaks at 1579 cm<sup>-1</sup> and 1501–1500 cm<sup>-1</sup> in the spectrum of P2ClAn protonated



**Figure 1** FTIR spectra of P2ClAn (a) protonated, (b) deprotonated, (c) reprotonated.



**Figure 2** P2ClAn/SiO<sub>2</sub> (a) protonated, (b) deprotonated, (c) reprotonated.

and reprotonated forms correspond to quinone- and benzene-ring stretching deformations, respectively [Figs. 1(a) and 1(c)]. The 1137 cm<sup>-1</sup> band is assigned to a vibration mode of the  $-NH^+$  structure, which is formed during protonation.<sup>26</sup>

When P2ClAn are treated with an alkali, the green conducting emeraldine deprotonated (Scheme 1) 1579 and 1500 cm<sup>-1</sup> modes in P2ClAn salts show a blue shift to 1581 and 1503 cm<sup>-1</sup> in the P2ClAn deprotonated [Fig. 1(b)]. The 1302 cm<sup>-1</sup> band is assigned to the C—N stretch of a secondary aromatic amine, whereas in the region of 1045–1006 cm<sup>-1</sup>, the aromatic C—H in-plane bending modes are usually observed. Out-of-plane deformations of C—H on trisubstituted rings are located in the region of 883–818 cm<sup>-1.27</sup> Additionally, it is seen that the intensity of band corresponding to quinoid ring at 1579 cm<sup>-1</sup> has decreased in emeraldine deprotonated form [Fig. 1(b)].

The spectra of the P2ClAn/SiO<sub>2</sub> nanocomposite in the presence of  $SiO_2$  [Figs. 2(a)–2(c)] differ from the spectra of P2ClAn forms. In the case of P2ClAn/ SiO<sub>2</sub> nanocomposite, the additional peaks at 1100 and 466 cm<sup>-1</sup> (characteristic of SiO<sub>2</sub>) appeared.<sup>20</sup> It is well known that in systems with polyaniline, strong guest-host interactions, such as hydrogen bonding, occur in the form of NH. . .nanomatrix.<sup>28</sup> In P2ClAn/SiO<sub>2</sub> structure, there is H-bonding interactions in form of N-H. . .O-Si- between P2ClAn and SiO<sub>2</sub>. These interactions have also been supported from shifting values in FTIR spectra. When P2ClAn/SiO<sub>2</sub> is treated with NH<sub>4</sub>OH, band at 1203  $cm^{-1}$  disappeared [Fig. 2(b)]. The intensities of the quinonoid band (1581 cm<sup>-1</sup>) and benzenoid band (1503 cm<sup>-1</sup>) are near to each other in P2ClAn/SiO<sub>2</sub> protonated form. However, in the spectrum of P2ClAn/ SiO<sub>2</sub> deprotonated form, the intensity of the quinonoid band decreases [Fig. 2(b)]. After the reprotonated process with HCl, its intensity increases according to deprotonated form of nanocomposite [Fig. 2(c)]. This indicates that the oxidation state of P2ClAn/ SiO<sub>2</sub> salts is higher than that of P2ClAn/SiO<sub>2</sub> deprotonated.

#### **UV-vis results**

P2ClAn and P2ClAn/SiO<sub>2</sub> in protonated, deprotonated, and reprotonated forms were solved into DMF, NMP, and H<sub>2</sub>SO<sub>4</sub>. Figures 3(a) and 3(b) show UV–vis spectra of P2ClAn and P2ClAn/SiO<sub>2</sub> deprotonated into NMP. As one can see, there are two major absorptions around 313–319 nm, which are related to the  $\pi \rightarrow \pi^*$  transition in the benzenoid structure<sup>29</sup> and the absorption at the wavelength 596–630 nm, which is ascribed to excitation formation in the quinonoid rings.<sup>30</sup>

All samples into H<sub>2</sub>SO<sub>4</sub> have shown three characteristic absorption bands 310–317, 520–536, and 748– 813 nm. The first absorption is due to the excitation of the nitrogen in the benzonoid segments ( $\pi \rightarrow \pi^*$ transition), while the second and the third ones are ascribed to polaron/bipolaron transition that occurs in protonated situation. All samples have shown two absorption bands into NMP and DMF whereas they exhibit three characteristic bands into H<sub>2</sub>SO<sub>4</sub>. NMP and DMF are basic enough to convert the protonated P2ClAn (ES) to the deprotonated P2ClAn (EB). However, all samples into H<sub>2</sub>SO<sub>4</sub> show characteristic emeraldine salt forms. Hence they have three absorption bands showing characteristic of ES.

The intensities of both Band I and Band II of all samples decrease with decreasing concentration of the solutions in all solvents. Figures 4(a)–4(b) show the absolute values of the absorbance for the benzenoid structure ( $A_B$ ) and quinonoid structure ( $A_Q$ ) of protonated and deprotonoted of P2ClAn/SiO<sub>2</sub>, i.e., the  $A_B$  and  $A_Q$  were plotted versus the concentration for all solvents.

It is evident that the concentration of the solution influences  $A_B$  more than it does  $A_{Q'}$  viz.  $A_B$  decreases faster than  $A_Q$  with decreasing concentration. Deprotonated forms of all samples have higher absorbance values than those of protonated forms for both benzenoid and quinoid units. This result shows that deprotonated forms of P2ClAn and P2ClAn/SiO<sub>2</sub> have better solubility than those of other forms.



**Figure 3** UV–vis spectra of (a) P2ClAn and (b) P2ClAn/SiO<sub>2</sub> deprotonated forms into NMP.



**Figure 4** Absolute values of the absorbance for the benzenoid structure (a) and quinonoid structure (b) of protonated and deprotonated forms of P2ClAn/SiO<sub>2</sub>.

The intensity ratio of  $A_Q/A_B$  were calculated from their UV–vis spectra. Figures 5(a)–5(f) correspond to  $A_Q/A_B$  values obtained for all forms of P2ClAn and P2ClAn/SiO<sub>2</sub> in various concentrations.

The ratio of intensities of  $A_Q/A_B$  is different from each into each solvent, especially into H<sub>2</sub>SO<sub>4</sub>. The intensity ratios of both P2ClAn and P2ClAn/SiO2 show a decrease with increasing solution concentration into NMP whereas they have not changing too much value into DMF. In H<sub>2</sub>SO<sub>4</sub> solvent, both the absorbance intensity of quinonoid and benzenoid rings have increased faster, and so the intensity ratio of  $A_Q/A_B$  into H<sub>2</sub>SO<sub>4</sub> also increased as different from others. Moreover, the polaron band addition to the benzenoid and guinonoid bands was observed for all polymers into H<sub>2</sub>SO<sub>4</sub> solvents. Here H<sub>2</sub>SO<sub>4</sub> has doped polymer chain because  $\lambda_2$  (nm), which contributed to polaron after doping and corresponded to localization of electron, shifted longer wavelength according to other solvents.

Table I shows maximum absorbance wavelengths of protonated, deprotonated, and reprotonated of P2ClAn and P2ClAn/SiO<sub>2</sub> (0.03 g/L) into all solvents. As can be seen from Table I,  $\lambda_2$  (nm) for P2ClAn/SiO<sub>2</sub> nanocomposite has shifted to shorter wavelength in its protonated, deprotonated, and reprotonated forms into DMF, NMP, and H<sub>2</sub>SO<sub>4</sub>.

#### **TGA results**

The thermal stability of  $P2ClAn/SiO_2$  composite has been investigated using thermogravimetric analysis. Figures 6(a)–6(c) depict the thermograms of SiO<sub>2</sub>,



**Figure 5** Intensity ratio of  $A_Q/A_B$  for all forms of P2ClAn and P2ClAn/SiO<sub>2</sub> into three solvents. (a) Protonated P2ClAn, (b) deprotonated P2ClAn, (c) reprotonated P2ClAn, (d) protonated P2ClAn/SiO<sub>2</sub>, (e) deprotonated P2ClAn/SiO<sub>2</sub>, (f) deprotonated P2ClAn/SiO<sub>2</sub>.

P2ClAn, and P2ClAn/SiO<sub>2</sub>, respectively. As indicated in the recent report<sup>31</sup> the onset decomposition temperatures of nanocomposites are higher than that of polymer and shifted towards the higher tempera-

ture range as the content of inorganic matrix. The decomposition temperatures obtained from thermograms are listed Table II. Initial decomposition temperatures confirm the increased thermal stability of

and Reprotonated of P2ClAn and P2ClAn/SiO <sub>2</sub> into All Solvents							
Sample	Structure	Solvent	λ <sub>1</sub> (nm)	λ <sub>2</sub> (nm)	λ <sub>3</sub> (nm)		
P2ClAn	Protonated	DMF	274	589	_		
P2ClAn/SiO <sub>2</sub>	Protonated	DMF	314	566	-		
P2ClAn	Deprotonated	DMF	311	596	-		
P2ClAn/SiO <sub>2</sub>	Deprotonated	DMF	318	567	-		
P2ClAn	Reprotonated	DMF	318	571	-		
P2ClAn/SiO <sub>2</sub>	Reprotonated	DMF	318	558	-		
P2ClAn	Protonated	NMP	308	623	-		
P2ClAn/SiO <sub>2</sub>	Protonated	NMP	318	611	-		
P2ClAn	Deprotonated	NMP	313	630	-		
P2ClAn/SiO <sub>2</sub>	Deprotonated	NMP	319	596	-		
P2ClAn	Reprotonated	NMP	324	636	-		
P2ClAn/SiO <sub>2</sub>	Reprotonated	NMP	318	572	-		
P2ClAn	Protonated	$H_2SO_4$	313	534	744		
P2ClAn/SiO <sub>2</sub>	Protonated	$H_2SO_4$	314	521	788		
P2ClAn	Deprotonated	$H_2SO_4$	315	534	758		
P2ClAn/SiO <sub>2</sub>	Deprotonated	$H_2SO_4$	316	521	787		
P2ClAn	Reprotonated	$H_2SO_4$	317	534	779		
P2ClAn/SiO <sub>2</sub>	Reprotonated	$H_2SO_4$	315	522	785		

TABLE I Maximum Absorbance Wavelengths of Protonated, Deprotonated, and Reprotonated of P2CIAn and P2CIAn/SiO<sub>2</sub> into All Solvents



Figure 6 TGA curve of (a) SiO<sub>2</sub>, (b) P2ClAn, (c) P2ClAn/SiO<sub>2</sub>.

composite. Also, the residual weight of composites is much higher than that of P2ClAn. Thus, these data readily exhibited the enhanced thermogravimetric stability for the P2ClAn/SiO<sub>2</sub> composite relative to P2ClAn.

#### X-ray results

Crystallinity and orientation of conducting polymer are of much interest because the more highly ordered systems could display a metallic-like conductive state. X-ray powder diffraction measurements exhibited that the pattern of as-received  $SiO_2$  [Fig. 7(a)] is typical for SiO2.32 The pure P2ClAn has typical pattern [Fig. 7(b)] for amorphous conducting polymer.<sup>33</sup> The X-ray diffraction pattern of P2ClAn/SiO<sub>2</sub> composite is shown in Figure 7(c). It has similar profile as observed in pure P2ClAn, indicating that the crystal structure of SiO<sub>2</sub> was not modified by P2ClAn. Also, these results indicate that P2ClAn is amorphous in the nanocomposite, which suggests that the addition of SiO<sub>2</sub> nanoparticles impedes the crystallization of the P2ClAn molecular chain. When P2ClAn is absorbed on the surface of the SiO<sub>2</sub> nanoparticles, the molecular chain of the absorbed P2ClAn is confined, and the degree of crystallinity decreases.<sup>34</sup>

# SEM and ESEM—conductivity, magnetic susceptibility results

The compatibility between the organic polymer and silica has a great effect on the thermal, mechanical, and optical properties of the hybrid materials. Figure 8(a) shows the SEM images of the as-received SiO<sub>2</sub>. It can be seen that SiO<sub>2</sub> are spherical and diameter of particle is at nanometer level. In the SEM photography, aggregation of silica was not observed. The fracture surface was very dense. P2ClAn shows particular morphology which is relatively uniform

TABLE II Thermal Degradation Temperatures of Samples

0	1		1	
$T_i^*$	$T_m$	$T_f$	Residue %	
(°C)	(°C)	(°Č)	at 800°C	
154	490	822	75	
111	476	835	0	
155	468	778	10	
		$\begin{array}{c c} \hline T_i^* & T_m \\ (^{\circ}C) & (^{\circ}C) \\ \hline 154 & 490 \\ 111 & 476 \\ 155 & 468 \\ \hline \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	





Figure 7 XRD pattern of (a) P2ClAn, (b) SiO<sub>2</sub>, (c) P2ClAn/SiO<sub>2</sub>.

[Fig. 8(b)]. After in situ polymerization reaction, P2ClAn/SiO<sub>2</sub> composite indicates that SiO<sub>2</sub> particles have a nucleus effect and caused a homogeneous structure in composite [Fig. 8(e)]. P2ClAn was preferentially formed on the surfaces of the SiO<sub>2</sub> particles during chemical oxidative polymerization of 2ClAn in the presence of the particles, resulting in core-shell structured composite particles. The dimension and morphology of SiO<sub>2</sub> changed after polymerization of 2ClAn onto SiO<sub>2</sub> surface. The SiO<sub>2</sub> particles would be present not only on composite particles surface but also distributed through their interior, a situation quite similar to that reported elsewhere.<sup>10,12</sup> The dispersion of the silica in the polymer matrix was also observed with ESEM. It can be seen from ESEM image (Fig. 9) that P2ClAn/SiO<sub>2</sub> composite has diameter of less than 1 µm. Additionally, the surface morphologies of P2ClAn and P2ClAn/SiO<sub>2</sub> were investigated with SEM after protonated, deprotonoted, and reprotonoted processes, respectively [Figs. 8(d)-8(g)].

After reprotonated process of P2ClAn, dimensions of granules have increased than that of P2ClAn deprotonated. The similar change has been observed in the structure of P2ClAn/SiO<sub>2</sub> composites. As can be seen from Figure 8(c), P2ClAn/SiO<sub>2</sub> reprotonated have bigger granular dimensions than its deprotonated structure [Fig. 8(b)].

The electrical conductivity of the P2ClAn and P2ClAn/SiO<sub>2</sub> were described as  $4.6 \times 10^{-7}$  and  $1.3 \times 10^{-5}$  S cm<sup>-1</sup>. The conductivity of the P2ClAn/ SiO<sub>2</sub> composite is higher than that of P2ClAn. Similar phenomenon was also found for PAni/TiO<sub>2</sub>, PAni/WO<sub>3</sub>, and PAni/clay composites.<sup>8,11,35</sup> The increase in conductivity would be due to the increase of efficiency of charge transfer between SiO<sub>2</sub> and polymer chains. SiO<sub>2</sub> might be increase protonation effect of polymer. Moreover, UV-vis results of all samples into H<sub>2</sub>SO<sub>4</sub> solvent exhibited that for P2ClAn/SiO<sub>2</sub>,  $\lambda_3$  value leads to increase of conjugation length and brings about the increase of conductivity. Protonation in P2ClAn/SiO2 would lead to the formation of radical cations by an internal redox reaction, causing reorganization of electronic structure to produce semiquinone radical cations, and accordingly the conductivity would be enhanced. Also, SEM images showed that P2ClAn/SiO<sub>2</sub> composite has homogenous morphology supporting good conductivity.

The magnetic properties of the composites have been considered by measuring magnetic susceptibility. The mass susceptibility values of samples were calculated from Gouy balance measurements. The mass susceptibility values of P2ClAn, SiO<sub>2</sub> and P2ClAn/SiO<sub>2</sub> are (+)  $3.25 \times 10^{-9}$ , (-)  $4.00 \times 10^{-9}$ , and (+)  $3.6 \times 10^{-9}$  (SI). SiO<sub>2</sub> has diamagnetic prop-



**Figure 8** SEM micrographs of (a) SiO<sub>2</sub>, (b) protonated P2ClAn, (c) deprotonated P2ClAn, (d) reprotonated P2ClAn, (e) protonated P2ClAn/SiO<sub>2</sub>, (f) deprotonated P2ClAn/SiO<sub>2</sub>, (g) deprotonated P2ClAn/SiO<sub>2</sub>.

erties. P2ClAn/SiO<sub>2</sub> nanocomposite shows mass susceptibility similar to that of P2ClAn due to P2ClAn absorbed on the surface of the SiO<sub>2</sub> nanoparticles. These results are compatible with results of X-ray. The charge carriers in composite produced upon doping are single charged polarons with spin  $\frac{1}{2}$ , which are the origin of magnetic susceptibility.<sup>36</sup>

#### CONCLUSIONS

P2ClAn and P2ClAn/SiO<sub>2</sub> were synthesized by *in situ* chemical oxidative polymerization method using  $(NH_4)_2S_2O_8$  oxidant. The conductivity of composite can be designed to be higher than that of P2ClAn. The TGA results confirm the enhanced thermal stability relative to P2ClAn. UV–vis properties of P2ClAn and P2ClAn/SiO<sub>2</sub> composite were investigated into three different solvents. Their protonated, deprotonated and reprotonated forms were used for UV–vis measurements. They exhibited interesting properties both in their all forms and solvents. The

changes in optical spectra had to be considered if practical applications of such materials are envisaged. P2ClAn/SiO<sub>2</sub> exhibited a better thermal stability regarding to P2ClAn. The conductivity and solu-



Figure 9 ESEM micrograph of P2ClAn/SiO<sub>2</sub>.

bility of P2ClAn were increased preparing P2ClAn/SiO<sub>2</sub>. Such processible composites will be promising candidates for advanced materials to be used in the high technology industries in the future.

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