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## High Yield Polymerisation of Aniline and Pyrrole in Presence of Montmorillonite Clay and Formation of Nanocomposites Thereof

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Considerable research attention was paid during the last decade on synthesis and evaluation of clay–polymer nanocomposites. Of the various techniques explored for such preparations impregnation of monomers followed by polymerization was used for a variety of monomers. Thus monomers like acrylonitrile, styrene, butadiene, methylmethacrylate etc were impregnated into clays and were polymerized in presence of free radical initiators.<sup>1</sup> Since the adsorption of monomer molecules between the clay lamellae was dependent on the dipole-moment of the monomer molecule, the yields of the physically inserted polymers were found to be low in general.<sup>2–6</sup>

In this context we wish to report that we have achieved high yield polymerization of aniline (ANI) and pyrrole (PY) in presence of montmorillonite (MMT) clay without the addition of any extraneously added oxidants like FeCl<sub>3</sub> or (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.<sup>7</sup>

Earlier, Biswas and SinhaRoy reported<sup>8</sup> that the polymerization of N-vinylcarbazole (NVC) monomer could be induced in presence of MMT in bulk (NVC, MMT, 68 °C) and under reflux condition using CHCl<sub>3</sub> solvent without any externally added oxidant. It was also observed by these workers that the melt interaction or solvent polymerization of NVC in presence of MMT involved intercalation of the polymer in the MMT lamellae which was confirmed by the manifestation of a d-spacing of 14.04 Å in the XRD scan of the PNVC (polyN-vinylcarbazole)–MMT composite. Subsequently, attempts of these authors<sup>9,10</sup> to polymerize ANI or PY under these conditions in presence of externally added oxidants (FeCl<sub>3</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) led to the formation of polyaniline (PANI) or polypyrrole (PPY) which were not intercalated in the MMT lamellae and existed only as surface-adsorbed polymers. On the other hand, Mehrotra and Giannelis<sup>11,12</sup> prepared highly oriented multi-layered PANI films by intercalative polymerization of ANI in a synthetic

mica type silicate Cu fluorohectorite from liquid phase (or vapour phase). Gallery Cu<sup>2+</sup> ions introduced by an ion-exchange process, served as the oxidation centers for the polymerization of ANI.

In this background the results of the present study appear to be particularly significant and provide some useful new information concerning the general field of clay–polymer interaction. The preparation, structural characterization and evaluation of some selective bulk properties of PANI–MMT and PPY–MMT composites are described in this article.

### EXPERIMENTAL

#### *Materials*

Aniline (Merck KGaA, Germany) and Pyrrole (Aldrich Chemical Company, Inc., USA) were freshly distilled under reduced pressure and stored in dark before use. MMT-K 10 (Aldrich Chemical Company, Inc., USA) was dried under vacuum for 2 h before use. All other reagents were of AR grade and used after necessary purification.

#### *Polymerization of ANI and PY*

A known amount of MMT was taken in a Pyrex flask fitted with a reflux condenser through which cold water was circulated. A known volume of ANI or PY monomer was added to the system. The reaction mixture was gradually heated (without any solvent) which resulted in a change of the colour of the mixture from red-brown to violet-black for the ANI system and lightblue-green-darkgreen and to black for the PY system respectively. Thereafter, the systems were kept under reflux for 3 h. The separated mass was shaken with excess methanol to remove any unreacted ANI or PY monomer and subsequently filtered. The black mass thus formed in either system was again repeatedly washed with methanol and finally dried at 50 °C un-

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der vacuum for 5 h to constant weight. A notable significant feature of these systems was that no PANI or PPY was formed when PY or ANI was injected into a suspension of MMT clay in water under sonication. This procedure was similar to that used for the preparation of various nano-oxide ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{SnO}_2$ ,  $\text{MnO}_2$  etc.) based composites of PANI or PPY except that  $\text{FeCl}_3/(\text{NH}_4)_2\text{S}_2\text{O}_8$  oxidants were used in these systems.<sup>13–19</sup>

#### Characterization

FTIR spectra of PANI–MMT and PPY–MMT composites were taken on a Perkin-Elmer Model 883 instrument. Thermogravimetric studies were performed on a Shimadzu DT 40 instrument. For SEM analyses, samples were sputter coated with gold layers and photographs were taken on a scanning electron microscope model Hitachi S 415 A. Transmission electron micrographic studies were performed on a Hitachi H 600 model instrument with composite samples in *iso*-propanol (4000 ppm) and dried on a copper grid. XRD patterns for various composites were obtained on a Philips Analytical X-Ray Diffractometer (PW 1710 BASED, Cu Anode, 40 kV, 20 mA). The DC conductivity values of the different composites were measured by conventional 4-probe method using pellets.

## RESULTS AND DISCUSSION

#### General Features of Polymerization

Table I summarizes some typical data on the poly-

merization of ANI and PY in presence of MMT clay. Keeping the monomer amount constant as the amount of MMT was increased the total yield of the composite as well as the percentage conversion to polymer was also increased in both ANI–MMT (entries 1–2, 4–7) and PY–MMT (entries 10–11, 13–16) systems. Entries 2–3, 7–8 (ANI–MMT) and entries 11–12, 16–17 (PY–MMT) indicate that keeping the MMT amount constant as the amounts of the monomers were increased, the percentage conversion to polymer was decreased in either system. The main feature of these polymerizations was that yields as high as 85% (for PANI) and 93% (for PPY) could be realized in these systems in 3 h.

#### FTIR Spectral Characteristics

The PANI–MMT composite revealed peaks at 3379 (>NH stretching); 1475–1602 (N–H bending); 1309 (C–N stretching)  $\text{cm}^{-1}$  and the PPY–MMT composite revealed peaks at 2320 (aromatic ring vibration of PY); 1043–1338 (C–H vibration of 2,5 substituted PY); 798 (C–H deformation of 2,5 di-substituted PY)  $\text{cm}^{-1}$  which matched with the corresponding reported values for PANI<sup>20</sup> and PPY<sup>21</sup> homopolymers respectively. The appearance of characteristic peaks for MMT (470, 525, 1045  $\text{cm}^{-1}$ )<sup>22</sup> was found to be common in both the spectra. Thus FTIR spectral studies clearly endorsed the presence of PANI or PPY along with MMT in either composite systems.

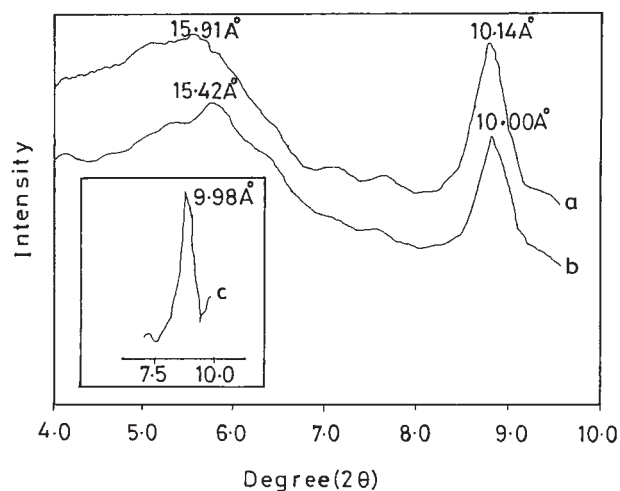
#### PANI/PPY–MMT Nanocomposite Formation

Our experiments clearly indicated that the polymer-

**Table I.** Some typical data for the polymerizations of ANI and PY by MMT.

Entry no.*	Monomer (g)	MMT (g)	% yield		
			Composite	Polymer	Polymer/gm of composite
1	0.2	0.25	60	10	7
2	0.2	0.50	81	35	12
3	0.5	0.50	58	16	14
4	0.2	0.75	92	60	14
5	0.2	1.00	94	65	11
6	0.2	1.25	96	70	10
7	0.2	1.50	98	85	10
8	0.5	1.50	89	55	16
9	0.2	0.50		15	6
10	0.2	0.25	65	21	14
11	0.2	0.50	83	41	14
12	0.5	0.50	60	18	15
13	0.2	0.75	93	67	15
14	0.2	1.00	95	72	12
15	0.2	1.25	97	77	11
16	0.2	1.50	99	93	11
17	0.5	1.50	91	62	17
18	0.2	0.50		20	7

\*Entries 1–9 and 10–18 for ANI–MMT and PY–MMT systems respectively.



**Figure 1.** XRD patterns for (a) PANI-MMT; (b) PPY-MMT and (c) MMT.

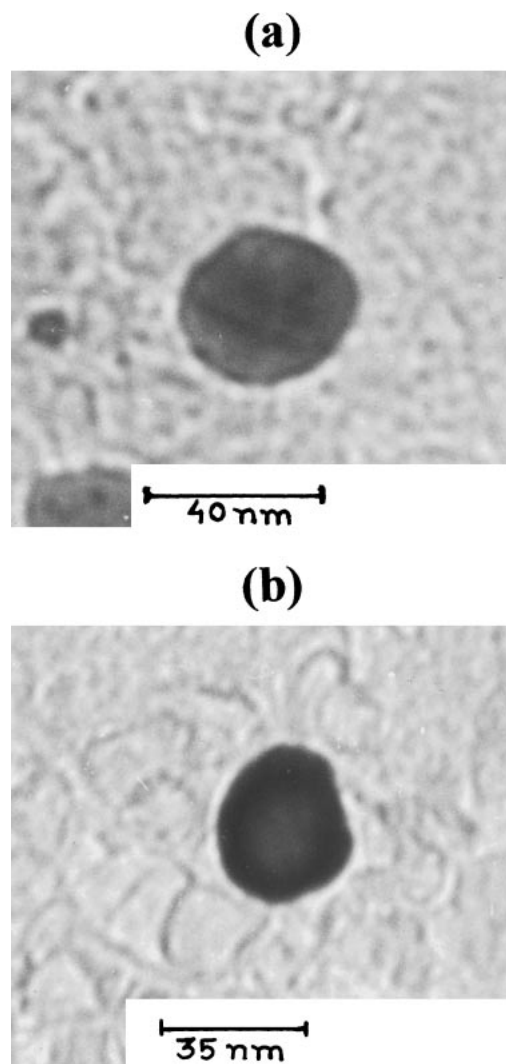
ization occurred when ANI or PY were kept in contact with MMT at temperatures  $>$  reflux temperature for both the liquid monomers. PANI or PPY were not formed by simply stirring the monomers into a suspension of MMT in water at higher temperature. Thus, these features suggested that oxidative polymerization of ANI or PY must have been induced after intercalation of ANI or PY in the MMT layers and subsequent interaction of these moieties with the sorbed cations present in MMT. This process would evidently lead to the formation of nanocomposites of PANI-MMT and PPY-MMT. This view appeared to be endorsed by the results of XRD and TEM analyses of these composites discussed below.

#### X-Ray Diffraction Characteristics

X-Ray diffraction intensity versus  $2\theta$  scans for PANI-MMT, PPY-MMT and MMT are shown in Figures 1a, 1b and 1c respectively. As it is well known appearance of a peak at  $9.98 \text{ \AA}$  for MMT was due to d-spacing in unintercalated MMT layers (interlayer distance).<sup>1</sup> For the composites, appearance of peaks at  $10.14 \text{ \AA}$  and  $10.00 \text{ \AA}$  for PANI-MMT and PPY-MMT respectively corresponded to d-spacing of any unintercalated MMT in the composites. Manifestation of peaks at  $2\theta = 5.72$  corresponding to a d-value  $15.91 \text{ \AA}$  and at  $2\theta = 5.50$  corresponding to a d-value  $15.42 \text{ \AA}$  for PANI-MMT and PPY-MMT systems respectively was suggestive of the intercalation of the polymer moieties in the MMT lamellae.

#### Transmission Electron Micrographic Characteristics

Transmission electron micrographs of MMT dispersion revealed presence of stringy particles.<sup>1,9</sup> In contrast, PANI-MMT and PPY-MMT composite dispersions showed formation of spherical particles. Magnified TEM images of a narrow section of



**Figure 2.** TEM images for (a) PANI-MMT and (b) PPY-MMT composites.

PANI-MMT and PPY-MMT composite dispersions were taken (Figures 2a and 2b respectively) to understand how the spherical polymers were accommodated in the MMT lamellae. The micrographs clearly revealed the intercalation of spherical PANI ( $\sim 40 \text{ nm}$ ) and PPY ( $\sim 35 \text{ nm}$ ) moieties in between the MMT layers.

#### Scanning Electron Micrographic Characteristics

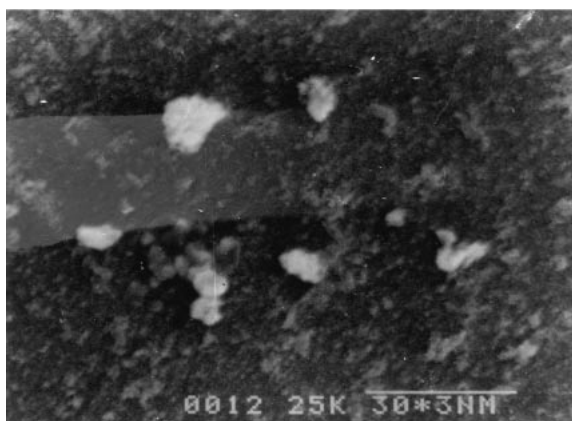
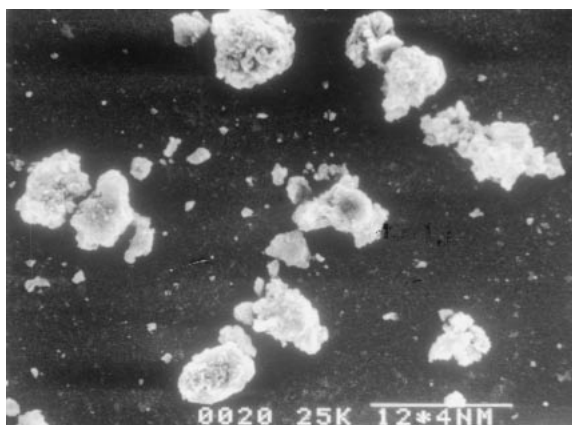
Figures 3a and 3b show the scanning electron micrographs of PANI-MMT and PPY-MMT composites respectively. The formation of lumps comprising densely packed aggregates of clay and polymer particles was detected in the SEM photographs. The average sizes of these lumps were  $23 \text{ nm}$  and  $37 \text{ nm}$  for PANI-MMT and PPY-MMT composites respectively.

#### Thermal Stability Characteristics

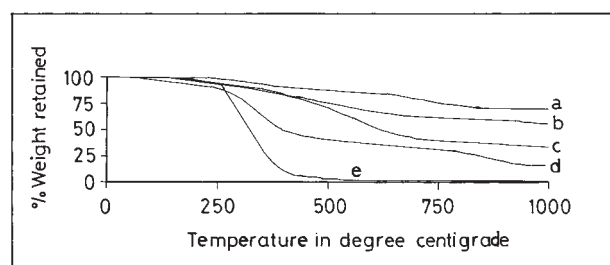
Figure 4 presents TG scans for (a) MMT, (b) PPY-

**Table II.** Conductivity data of various PANI and PPY based composite systems.

Entry no.	System	Oxidant	DC conductivity (S/cm)	Reference
1	PANI–MMT	—	$10^{-5}$	This study
2	PANI–MMT	$(\text{NH}_4)_2\text{S}_2\text{O}_8$ or $\text{FeCl}_3$	$10^{-1}$ – $10^{-3}$	10
3	PANI– $\text{SiO}_2/\text{ZrO}_2/\text{MnO}_2$	$(\text{NH}_4)_2\text{S}_2\text{O}_8$ or $\text{FeCl}_3$	$10^{-3}$	14–19
4	PPY–MMT	—	$10^{-6}$	This study
5	PPY–MMT	$\text{FeCl}_3$	$10^{-1}$ – $10^{-5}$	9
6	PPY– $\text{SiO}_2/\text{ZrO}_2/\text{MnO}_2$	$\text{FeCl}_3$	$10^{-5}$	14–19

**Figure 3.** SEM photographs for (a) PANI–MMT and (b) PPY–MMT composites.

MMT, (c) PANI–MMT, (d) PPY and (e) PANI respectively. The trend in the order of overall stability was MMT > PPY–MMT > PPY and MMT > PANI–MMT > PANI. The stability of MMT was appreciably higher than those for PANI–MMT or PANI homopolymer and PPY–MMT or PPY homopolymer. However, the fall in the stability of the polymer loaded MMT was evidently due to the loss of the less stable polymer moieties from the MMT matrix. On the other hand, the thermal stability of the corresponding MMT based composites was higher with respect to the stability of PANI or PPY as a result of incorporation

**Figure 4.** TG scans for (a) MMT; (b) PPY–MMT; (c) PANI–MMT; (d) PPY and (e) PANI.

of more thermally stable MMT moieties in those composites.

#### Conductivity

DC conductivity values for PANI–MMT ( $10^{-5}$  S/cm) and PPY–MMT ( $10^{-6}$  S/cm) as realized in the present study were relatively lower than those realized with the nanooxide based composites of these homopolymers (Table II). However, these later systems used external oxidants like  $\text{FeCl}_3/(\text{NH}_4)_2\text{S}_2\text{O}_8$  which might in addition behave as dopants thereby improving the conductivity values.

#### Mechanism of Polymerizations of ANI and PY

As it is well known, MMT has a layered structure in which sorbed cations are present in between the silicate layers. Interlayer distance is 10.00 Å as revealed by the XRD pattern of MMT. MMT reportedly exhibits dual acidic properties—Lewis and Bronstead—depending on the conditions used. Sorbed cations are usually coordinated to  $\text{H}_2\text{O}$  molecules, the coordination number depending on the nature of the sorbed cations.<sup>2</sup>

The distinct change in the colour of the reaction mixture comprising MMT and intercalated ANI or PY moieties (at reflux temperature) was indicative of charge-transfer-reaction between the sorbed cations in MMT and ANI/PY leading to the formation of  $[\text{ANI}]^{\bullet+}$  or  $[\text{PY}]^{\bullet+}$  (active species for charge-transfer-polymerization). Propagation could then follow

the usual pathway via the interaction of [ANI]<sup>•</sup> or [PY]<sup>•</sup> with fresh [ANI] or [PY] moieties respectively.<sup>7,23</sup>

At room temperature, the percentage conversion to PANI and PPY was 15 (entry 9, Table I) and 20 (entry 18, Table I) respectively. Evidently, at lower temperature sorbed cations would be mostly coordinated to H<sub>2</sub>O molecules but at higher temperature [ANI] or [PY] moieties could replace the water molecules and coordinate to the same sorbed cation at a faster rate. High yield was realized because more than one monomer moiety could interact with the same sorbed cation at the same time depending on the coordination number and effective charge of the sorbed cation.

However, direct evidence of the proposed coordination would be difficult to find in the case of PANI/PPY–MMT systems because of the insoluble nature of the polymers. So we had refluxed a soluble compound with nitrogen (N) heteroatom–2-aminothiazole (2AT) with MMT in bulk and then washed off any uncoordinated 2AT by extraction with EtOH in which 2AT was very much soluble. The residual MMT was found to display the characteristic FTIR absorption for 2AT along with those for MMT. Similar adsorption of 2,4-dinitro-*o*-cresol (DNOC) and 4,6-dinitro-*o*-sec-butyl phenol (DINOSEB) herbicides by smectic clays and intercalation of these moieties in the clay matrix was reported by Boyd *et al.*<sup>24</sup>

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