

# Preparation and evaluation of a nanocomposite of polythiophene with Al<sub>2</sub>O<sub>3</sub>

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**Abstract:** The polymerization of thiophene (TP), in bulk and in solution in CHCl<sub>3</sub> by FeCl<sub>3</sub> resulted in the formation of a polymer which was characterized by FTIR as polythiophene (PTP). High yield was realized in the latter case. The polymerization of TP with FeCl<sub>3</sub> and nanodimensional Al<sub>2</sub>O<sub>3</sub> resulted in the formation of a nanocomposite which was partly dispersible in aqueous and non-aqueous media. The dispersibility appeared to be higher when the polymerization was conducted in a suspension containing a higher amount of Al<sub>2</sub>O<sub>3</sub>. Scanning electron micrographs showed globular particles and the presence of clusters of composite particles. Transmission electron micrographic (TEM) analyses revealed the particle size of the composite to be in the range 22–74 nm. Thermal analyses (TG/DTA) revealed the outstanding stability of PTP–Al<sub>2</sub>O<sub>3</sub> composites compared to that of PTP. The conductivity of PTP and of PTP–Al<sub>2</sub>O<sub>3</sub> composite was of the order of 10<sup>–3</sup> S cm<sup>–1</sup> for samples doped with I<sub>2</sub>.

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**Keywords:** nanocomposite; nanodimensional Al<sub>2</sub>O<sub>3</sub>; polythiophene; thermal stability; conductivity; water-dispersibility

## INTRODUCTION

Speciality polymers such as polypyrrole (PPY), polyaniline (PANI) and polythiophene (PTP) display outstanding conductivity and other interesting bulk properties, but suffer from processibility limitations due to their intractable nature. Much research attention has been paid globally to obtain processible dispersions of PPY and PANI in aqueous/non-aqueous solvents. Armes and co-workers<sup>1,2</sup> developed a variety of PPY- or PANI-based water dispersible nanocomposites using colloidal SiO<sub>2</sub> and SnO<sub>2</sub> as particulate dispersants. Biswas and Sinha Ray prepared conducting nanocomposites of poly(*N*-vinylcarbazole) (PNVC), PPY and PANI with montmorillonite clay (MMT),<sup>3–5</sup> SiO<sub>2</sub>,<sup>6</sup> MnO<sub>2</sub><sup>7</sup> and ZrO<sub>2</sub>.<sup>8</sup> To the best of our knowledge, no report seems to be available dealing with the preparation of water-dispersible PTP nanocomposites. A review by Roncali<sup>9</sup> refers to the work on some PTP-polymer [poly(methyl methacrylate), poly(vinyl chloride), polystyrene (PMMA, PVC, PS)] composites by direct electropolymerization of TP in the presence of the respective host polymer, and on other PTP composites using multistep methods. Besides these procedures, polymethylthiophene-metal (Ag, Pt, Cu, Pd) composites were prepared by electrodeposition.<sup>9</sup> More recently, *in situ* intercalative polymerizations of TP derivatives in host matrices such as FeOCl, zeolite or xerogels were reported.<sup>9</sup> With the above background, we became interested in developing composites of

PTP based on a nanodimensional metal oxide as the particulate dispersant, with the idea of making PTP dispersible in aqueous or non-aqueous solvents. In view of the insolubility of TP in water, conventional procedures such as injecting water soluble monomers into an aqueous dispersion of metal oxide containing FeCl<sub>3</sub>, as used by Armes and co-workers<sup>1,2</sup> or by us<sup>3–8</sup> in the case of PY or ANI based systems, could not be applied for the preparation of PTP-metal oxide composites. Yet another hurdle was the well-known fact<sup>10</sup> that, unlike PY, TP is more difficult to oxidize by FeCl<sub>3</sub>, which stands in the way of achieving high yields of PTP during chemical oxidative polymerization. However, we have now been able to develop a convenient procedure for the preparation of PTP in high yield in the presence of FeCl<sub>3</sub> as the oxidant. By applying this procedure, we have been able to prepare PTP–Al<sub>2</sub>O<sub>3</sub> nanocomposites. We wish to highlight in this paper the preparation, characterization and some evaluations of bulk properties of the composites, including their dispersibility in aqueous/non-aqueous media. Nanodimensional Al<sub>2</sub>O<sub>3</sub> was chosen as the dispersant because it was thought that its ultra-small size (≈10 nm) compared to other oxides commonly used, such as SiO<sub>2</sub>, SnO<sub>2</sub>, MnO<sub>2</sub> and ZrO<sub>2</sub>, might facilitate the formation of stable suspensions, our earlier studies having indicated that with lower particle size of MnO<sub>2</sub> (>10 nm), ZrO<sub>2</sub> (>10 nm), the tendency to form water dispersible PPY or PANI suspensions was somewhat facilitated.<sup>7,8</sup>

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Contract/grant sponsor: Council of Scientific and Industrial Research (CSIR), New Delhi; contract/grant number: 80(0037)/EMR II

(Received 23 October 2001; revised version received 18 March 2002; accepted 5 April 2002)

## EXPERIMENTAL

### Materials

Thiophene (Aldrich, USA) was freshly distilled under reduced pressure before use. Nanodimensional  $\text{Al}_2\text{O}_3$  powder was prepared in the National Metallurgical Laboratory, Jamshedpur, India, and kindly donated by this organization. All other reagents and chemicals were of analytical grade.

### Chemical polymerization of TP using $\text{FeCl}_3$

A known mass of TP was directly injected into a round-bottomed flask containing a known quantity of  $\text{FeCl}_3$ , and the reaction mixture was heated to  $60^\circ\text{C}$  under reflux for 3 h. The total contents were then washed thoroughly with methanol and water. The deep brownish-black powdery mass was dried at  $60^\circ\text{C}$  under vacuum. In a different procedure, a known mass of TP was placed in a conical flask containing 30 ml  $\text{CHCl}_3$  and to this a particular quantity of  $\text{FeCl}_3$  was added in one go. The reaction mixture was stirred for 3 h at room temperature. The product was washed thoroughly with methanol and water. The deep brownish-black mass was then dried at  $60^\circ\text{C}$  under vacuum.

### Preparation of composites

A known mass of  $\text{Al}_2\text{O}_3$  was finely dispersed in a conical flask containing 30 ml of  $\text{CHCl}_3$ , after which a known quantity of TP was injected. A particular amount of  $\text{FeCl}_3$  was then added to the solution in one go. The reaction mixture was magnetically stirred at room temperature for 3 h. The solution was centrifuged and the separated mass was thoroughly washed with methanol and water. The deep brownish-black mass was dried at  $60^\circ\text{C}$  under vacuum.

### Characterization and property evaluation

FTIR spectra of PTP and PTP- $\text{Al}_2\text{O}_3$  composites were taken on a Jasco 410 (Essex, UK) instrument.

The surface morphology of the composites was studied with a Hitachi S 415 A (Tokyo, Japan) scanning electron microscope. Particle sizes of the PTP- $\text{Al}_2\text{O}_3$  composite were measured by transmission electron microscopy (TEM) on a Hitachi 600 (Tokyo, Japan) instrument. TEM studies were conducted with a dilute dispersion of the composite in isopropanol dried on a copper grid. Thermogravimetric (TG) and differential thermal analysis (DTA) studies were conducted on a Shimadzu DT-40 (Tokyo, Japan) instrument. Direct current (DC) conductivity measurements were conducted on pressed pellets with silver coating.

## RESULTS AND DISCUSSION

Table 1 presents some data on the polymerization and composite formation in TP- $\text{FeCl}_3$ - $\text{CHCl}_3$  and TP- $\text{FeCl}_3$ / $\text{Al}_2\text{O}_3$ - $\text{CHCl}_3$  systems, respectively. It is generally accepted<sup>10</sup> that TP is more difficult to oxidize than PY, so that polymerization of TP by  $\text{FeCl}_3$  is not as facile as for PY- $\text{FeCl}_3$ . Miyata and co-workers<sup>11</sup> reported the preparation of highly conducting PTP and PPY in high yields in the presence of anhydrous  $\text{FeCl}_3$  by controlling the oxidation potential of the systems to an optimum value. We thus attempted to prepare PTP in high yield by using variable  $\text{FeCl}_3$ /TP ratios in  $\text{CHCl}_3$  medium, which would in principle change the oxidation potential of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple in the TP- $\text{FeCl}_3$  redox system.

Entries 1–7 in Table 1 record some polymerization data in TP- $\text{FeCl}_3$  polymerization systems in bulk and in  $\text{CHCl}_3$  solution. Entries 1 and 2 suggest that a high yield of PTP (70–80%) could be achieved when TP was added to  $\text{FeCl}_3$  directly at temperatures above  $60^\circ\text{C}$ . However, at room temperature the reaction was not as vigorous and the yield was low (not measurable). Overall, this procedure was rather clumsy and

Entry	Reaction conditions		Conversion (%)	Conversion per g of composite (%)	Particle size (nm)
	$\text{FeCl}_3$ /TP (w/w)	$\text{Al}_2\text{O}_3$ (g)			
1	7/1	–	70		22–74
2	8/1	–	80		
3	1/1	–	6		
4	2/1	–	12		
5	10/1	–	80		
6	12/1	–	106		
7	16/1	–	108		
8	1/1	0.1	8	6	
9	12/1	0.1	106	88	
10	16/1	0.1	126	105	
11	12/1	0.5	164	82	
12	14/1	0.5	172	86	
13	1/1	0.1 <sup>b</sup>	32	26	27–76
14	1.5/1	0.1 <sup>b</sup>	54	45	

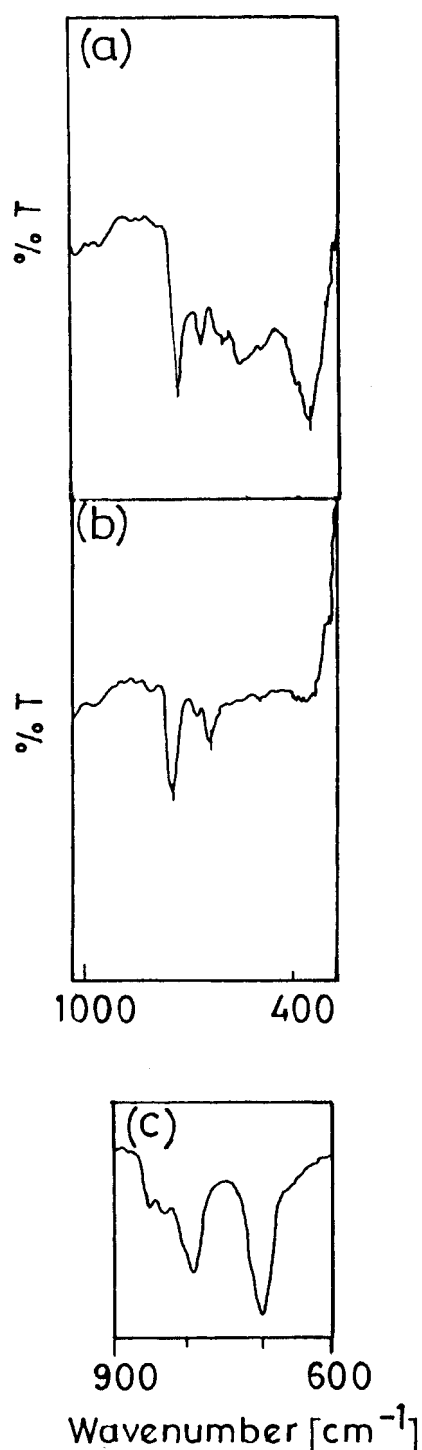
**Table 1.** Data on polymerization<sup>a</sup> and composite formation<sup>b</sup> in TP and TP- $\text{Al}_2\text{O}_3$  system respectively

<sup>a</sup> Experiments were conducted in bulk at  $60^\circ\text{C}$  for entries 1, 2, 13 and 14, and in  $\text{CHCl}_3$  (30 ml) for entries 3–12 at room temperature for 3 h.

<sup>b</sup>  $\text{Al}_2\text{O}_3$  was impregnated with  $\text{FeCl}_3$ .

the loss of unreacted TP was appreciable even though reflux conditions were used.

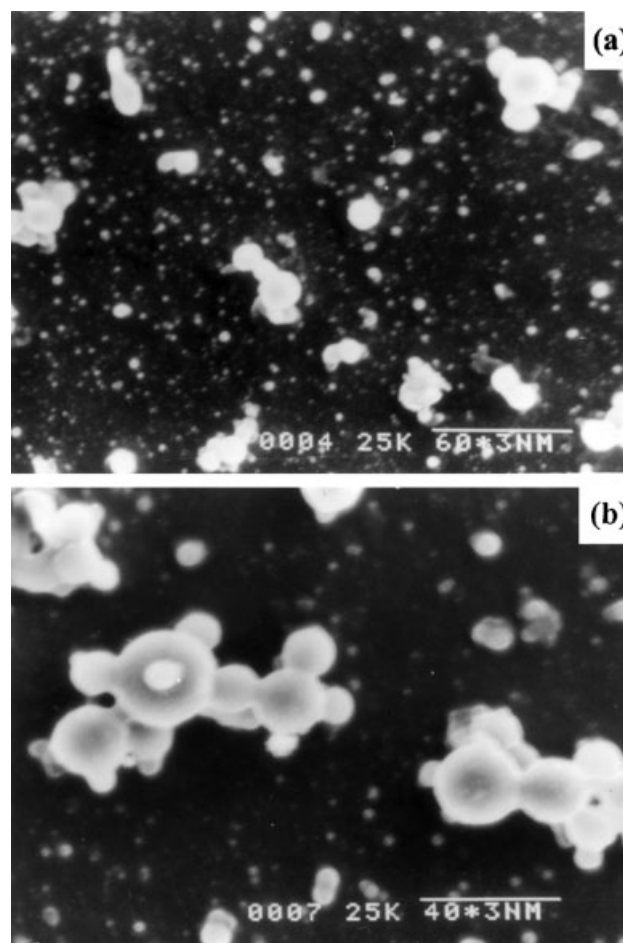
Entries 3–7 record some polymerization data using  $\text{CHCl}_3$  as the solvent. At a low  $\text{FeCl}_3/\text{TP}$  (wt/wt) ratio of 1/1 very poor yield of PTP was realized. With an increase in the  $\text{FeCl}_3/\text{TP}$  ratio, the yield of PTP started to increase progressively, up to complete conversion. These observations are significant in the sense that they endorse the formation of PTP in high yield in  $\text{CHCl}_3$  medium during chemical polymerization by anhydrous  $\text{FeCl}_3$ .



**Figure 1.** FTIR spectra of (a) PTP- $\text{Al}_2\text{O}_3$  composite; (b) PTP and (c) PTP obtained by  $\text{FeCl}_3 \cdot 3\text{H}_2\text{O}$  catalyst.

Entries 8–12 present some composite formation data using alumina as a nanodimensional metal oxide. As before, the yield of polymer was found to increase dramatically with increasing  $\text{FeCl}_3/\text{TP}$  ratio.

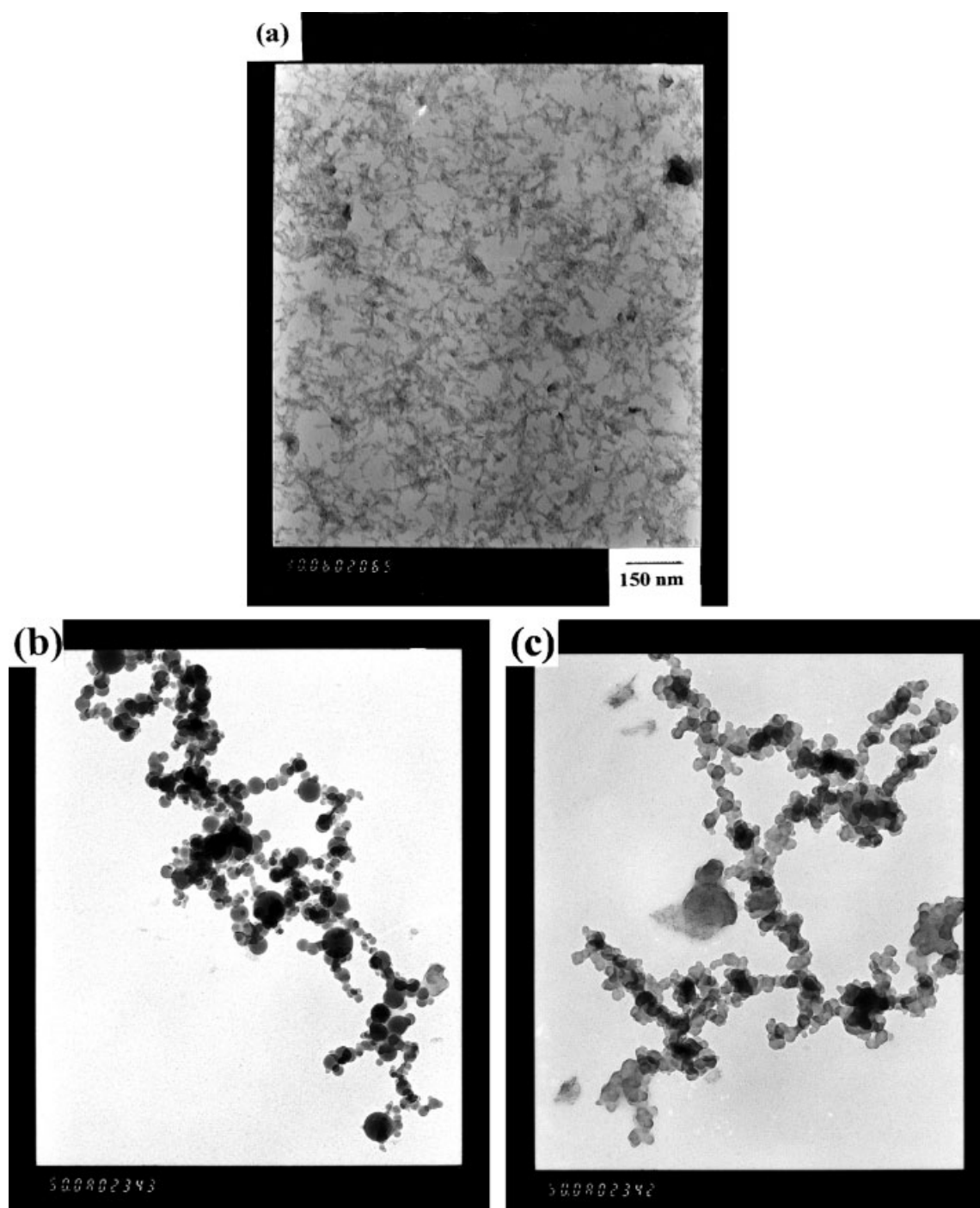
Entries 13 and 14 represent the polymerization yield achieved when the alumina was impregnated with  $\text{FeCl}_3$  by our earlier method<sup>4–6</sup> and the polymerization was conducted in bulk under reflux at 60 °C. However, these yields were lower than those realized in entries 1 and 2. Accordingly, the  $\text{FeCl}_3$  impregnation procedure did not prove very efficient compared to the presently adopted procedure involving dispersion of  $\text{Al}_2\text{O}_3$  in  $\text{CHCl}_3$  (entries 8–12). In general, entries 1–14 in Table 1 clearly indicate that the yield of PTP systematically varied with the  $\text{Fe}^{3+}$  loading in the initial feed. To achieve this high yield it was always necessary to add the entire amount of  $\text{FeCl}_3$  to the  $\text{CHCl}_3$ -TP solution in one go with constant stirring. If the  $\text{FeCl}_3$  was added gradually, high yields could not be obtained. Possibly, the former procedure was more appropriate for maintaining a high  $\text{Fe}^{3+}/\text{Fe}^{2+}$  balance around the TP moieties in the medium, and hence an enhanced oxidation potential, a condition believed<sup>11</sup> to be necessary for achieving high yield in the system. We want to emphasize that our procedure is indeed simple as far as the realization of high yield in chemical oxidative polymerization of TP by  $\text{FeCl}_3$  is concerned.



**Figure 2.** (a), (b) Scanning electron micrographs of PTP- $\text{Al}_2\text{O}_3$  composite.

The formation of PTP- $\text{Al}_2\text{O}_3$  composite (entries 8–12 in, Table 1) deserves some comment. As is well known, during the past decade a great deal of research attention has been paid to the preparation of water dispersible nanocomposites of speciality polymers such as PPY and PANI by using nanodimensional metal oxides, such as  $\text{MnO}_2$ ,<sup>7</sup>  $\text{ZrO}_2$ ,<sup>8</sup>  $\text{SiO}_2$ <sup>6</sup> and MMT clay<sup>3–5</sup> in aqueous medium, as particulate dispersants. The general procedure adopted for the polymerization of these water-soluble monomers was to add them into an aqueous suspension of the nanodimensional metal oxides in the presence of oxidants such as  $\text{FeCl}_3$  or  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ . The use of such a procedure for pro-

ducing dispersible PTP composites has not reportedly been attempted so far, evidently because of the general insolubility of TP in water and the relative inefficiency of  $\text{FeCl}_3$  in polymerizing TP in aqueous systems. However, Biswas and Sinha Ray<sup>6–8</sup> developed a method for the preparation of oxide based nanocomposites of PNVC by polymerizing *N*-vinylcarbazole (a monomer insoluble in water) in a non-aqueous solvent, in the presence of a Lewis acid  $\text{FeCl}_3$  as the initiator, and then precipitating PNVC by methanol addition to the medium containing the finely dispersed oxide particles. Thus, we decided to polymerize TP using  $\text{FeCl}_3$  in  $\text{CHCl}_3$  medium in which nanodimen-



**Figure 3.** Transmission electron micrographs of (a)  $\text{Al}_2\text{O}_3$  particles and (b) PTP- $\text{Al}_2\text{O}_3$  particles with  $\text{CHCl}_3$  and (c) without any solvent.

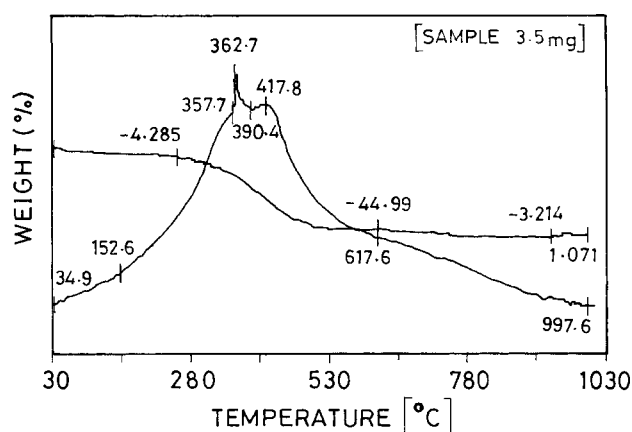


Figure 4. TG and DTA thermograms of a PTP- $\text{Al}_2\text{O}_3$  composite.

sional  $\text{Al}_2\text{O}_3$  powder had been finely dispersed by sonication. As expected, the resultant PTP, being insoluble in  $\text{CHCl}_3$ , precipitated out onto the  $\text{Al}_2\text{O}_3$  particles, thereby forming PTP- $\text{Al}_2\text{O}_3$  composite particles.

#### FTIR spectral characteristics

The formation of PTP and its incorporation in the composite were readily determined by the IR absorption peaks at  $695\text{ cm}^{-1}$  and  $786\text{ cm}^{-1}$  usually ascribed<sup>9,10</sup> to the C—H out-of-plane stretching vibration. For comparison, the reported IR spectrum of PTP prepared in  $\text{FeCl}_3 \cdot 0.5\text{H}_2\text{O}$  is presented in Fig 1 together with the corresponding peaks in the present system.

#### Scanning electron micrographic analyses

Scanning electron micrographs of a PTP- $\text{Al}_2\text{O}_3$  composite at two magnifications are presented in Fig 2. In general, the composite particles were characterized by globular morphology; also, particles were not of uniform size and exhibited a tendency to form clusters.

#### Transmission electron micrographic analyses

Transmission electron micrographs of  $\text{Al}_2\text{O}_3$  and some PTP- $\text{Al}_2\text{O}_3$  composites are shown in Fig 3. Figure 3(a) shows that the  $\text{Al}_2\text{O}_3$  particles exist as stringy particles (average size about 10 nm). The TEM image of the PTP- $\text{Al}_2\text{O}_3$  composite prepared in  $\text{CHCl}_3$  revealed the formation of globular clusters of polymer- $\text{Al}_2\text{O}_3$  particles. By contrast, PTP- $\text{Al}_2\text{O}_3$  composite prepared in the absence of any solvent showed

relatively irregular particle formation. The average particle diameters as evaluated from Fig 3(c) were in the range 27–74 nm.

#### Thermal stability of PTP- $\text{Al}_2\text{O}_3$ composites

Figure 4 shows the thermogravimetric stability data for the PTP- $\text{Al}_2\text{O}_3$  composite. The composite was initially stable up to  $250^\circ\text{C}$  (4.3% mass loss); thereafter it gradually lost mass (about 45%) up to  $617^\circ\text{C}$  and subsequently remained stable up to  $997^\circ\text{C}$  with 2% further mass loss. The total mass loss suffered by  $\text{Al}_2\text{O}_3$  was 34%, while over the same temperature range ( $997^\circ\text{C}$ ) PTP was initially stable up to  $248^\circ\text{C}$  and decomposed completely at  $600^\circ\text{C}$ . In fact, these observed trends served as proof for the presence of PTP together with  $\text{Al}_2\text{O}_3$  particles in the composite, because otherwise a repeat TG trend for PTP would actually have been observed in Fig 4. The DTA scan for PTP- $\text{Al}_2\text{O}_3$  revealed only a broad hump between 350 and  $420^\circ\text{C}$ , while the corresponding DTA for the base polymer revealed a sharp endothermic transition at  $433^\circ\text{C}$ . Thus, these data confirm the enhanced thermogravimetric stability of the PTP- $\text{Al}_2\text{O}_3$  composite relative to that of PTP.

#### Conductivity characteristics

Table 2 compares the conductivity values of PTP and PTP- $\text{Al}_2\text{O}_3$  composites with some of the PTP conductivities reported in the literature. In this study, PTP and PTP- $\text{Al}_2\text{O}_3$  composites were doped with  $\text{I}_2$  for a week. However, as suggested by Table 2, wide variations are actually observed between the various values reported, particularly that of Miyata and co-workers.<sup>11</sup> This seems to be due to some inherent structural defects<sup>11</sup> of the PTP produced by chemical oxidative polymerization.

#### Dispersibility of PTP and PTP- $\text{Al}_2\text{O}_3$ composites in aqueous and non-aqueous solvents

Table 3 summarizes the conditions applied to obtain dispersions of PTP and PTP- $\text{Al}_2\text{O}_3$  composites in aqueous medium. Evidently, PTP was not dispersible under any of the conditions applied. Significantly, the PTP- $\text{Al}_2\text{O}_3$  composite showed some tendency to exist as a stable suspension in water and in isopropanol. A comparison of entries 3 and 4 in Table 3 suggests that the higher the quantity of  $\text{Al}_2\text{O}_3$  in the initial feed, the greater the tendency of the particles to disperse in the medium.

Table 2. Direct current conductivity of PTP and PTP- $\text{Al}_2\text{O}_3$  composites

Polymer (reaction conditions)	Dopant	Conductivity ( $\text{S cm}^{-1}$ )	Reference
PTP ( $\text{CHCl}_3$ - $\text{FeCl}_3$ )	$\text{I}_2$ , 1 week	$0.3 \times 10^{-3}$	This study
PTP- $\text{Al}_2\text{O}_3$ ( $\text{CHCl}_3$ - $\text{FeCl}_3$ )	$\text{I}_2$ , 1 week	$0.4 \times 10^{-3}$	This study
PTP ( $\text{CHCl}_3$ - $\text{FeCl}_3$ - $3\text{H}_2\text{O}$ )		$4.3 \times 10^{-4}$	10
PTP ( $\text{AsF}_5$ , pressure)		$2 \times 10^{-2}$	9
PTP ( $\text{CHCl}_3$ - $\text{FeCl}_3$ )	$\text{I}_2$ , 1 week	70	11
PTP (vapour- $\text{FeCl}_3$ )		14	10

**Table 3.** Water dispersibility of PTP and PTP–Al<sub>2</sub>O<sub>3</sub> based composites

Entry	Conditions	Observation
1	Bulk PTP (entries 1 and 2, Table 1) sonicated in water for 1 h	Immediate precipitation of polymer. No colouration of the supernatant solution
2	PTP (entries 3–7, Table 1) sonicated in water for 1 h	Gradual settling down of suspended polymer. No colouration of the supernatant solution
3	PTP–Al <sub>2</sub> O <sub>3</sub> composite (entries 8–10, 13 and 14 Table 1) sonicated in water/isopropanol for 1 h	A deep brown dispersion of polymer was formed which was stable for more than a month. Part of the polymer settled down which could again be sonicated with a fresh quantity of water to produce a brown dispersion, a part remaining insoluble, and so on
4	PTP–Al <sub>2</sub> O <sub>3</sub> composite with higher percentage of Al <sub>2</sub> O <sub>3</sub> (entries 11 and 12, Table 1) sonicated in water for 1 h	The observation was similar to that for entry 3 except that a relatively smaller amount of the composite particles settled down

## CONCLUSIONS

This work establishes the conditions for the preparation of (1) PTP homopolymer in high yield by FeCl<sub>3</sub> initiator in CHCl<sub>3</sub> medium and (2) PTP–Al<sub>2</sub>O<sub>3</sub> nanocomposites partly dispersible in aqueous medium. The PTP–Al<sub>2</sub>O<sub>3</sub> nanocomposites showed improved thermogravimetric stability compared to PTP homopolymer, while the conductivity of either polymer was of the order of 10<sup>−3</sup> S cm<sup>−1</sup>.

## ACKNOWLEDGEMENTS

The authors are grateful to the Council of Scientific and Industrial Research (CSIR), New Delhi, India, for funding a project no 80(0037)/EMR II to MB, to Prof S Ghosh, Head of the Department of Chemistry, Presidency College, Calcutta, to the Principal, Presidency College, Calcutta for facilities, to Dr HS Maiti, Director, Central Glass and Ceramic Research Institute, Jadavpur, Calcutta for help in conductivity

measurements and many helpful discussions, and to Mr P Roy and A Chakraborty of the Saha Institute of Nuclear Physics for TEM analyses.

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