

# Polymer-Supported Heterogeneous Titanium-Based Ziegler-Natta Catalyst for Ethylene Polymerization

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Received 16 June 2011; accepted 11 October 2011

DOI 10.1002/app.36347

Published online 29 January 2012 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Reported here in, is the synthesis of polystyrene (PS)-supported Ziegler–Natta catalyst (PS-TiCl<sub>4</sub>) by the reaction of PS and titanium tetrachloride (TiCl<sub>4</sub>). PS was synthesized by emulsion polymerization using super critical CO<sub>2</sub> (sc-CO<sub>2</sub>) as a medium. Three catalysts were synthesized by varying the TiCl<sub>4</sub>/PS weight ratio in hexane medium. The resulting catalysts were characterized by Fourier transformed-infrared spectroscopy, UV–visible spectroscopy, scanning electron microscope and energy dispersive X-ray detector, X-ray diffraction analysis. The acidity of the catalysts in an acetone/water solution was measured by pH meter. The thermogravimetric analysis reveals that catalysts

are stable upto 150–180°C. Due to their higher degree of thermal stability these catalysts may potentially be used as a support in conventional Ziegler–Natta catalyst for ethylene polymerization. These catalysts also showed good storability and its overall catalytic productivity are found to be 3720 g PE/g Ti. The productivity of the catalysts also depended on the titanium concentration in the polymer matrix. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2539–2548, 2012

**Key words:** Ziegler–Natta; polystyrene; polymer-supported catalysts; slurry ethylene polymerization; catalyst activity and catalyst storability

## INTRODUCTION

The worldwide consumption of polyolefin or polymers made from alkenes monomers, such as ethylene, propylene, 1-butene, 1-hexene, etc. have grown to 140 million ton per year till date, comparing to the 60% of the total worldwide thermoplastic market. Each year 10 million tons of polyethylene (PE) is being produced throughout the world with the supported Ziegler–Natta catalyst.<sup>1,2</sup>

To increase the activity of Ziegler–Natta catalyst MgCl<sub>2</sub> is used as a support. MgCl<sub>2</sub>-supported Ziegler–Natta catalyst possess high catalytic activity (productivity 100 kg PE/g of titanium) and opened a new era both from the industrial and the scientific point of view.<sup>3,4</sup> In addition to MgCl<sub>2</sub>, many inorganic supports such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MCM-41, and mesoporous silica fiber have been developed and used in olefin polymerization.<sup>5–7</sup> Interestingly, MgCl<sub>2</sub>-supported Ti-based Ziegler–Natta catalyst shows amazingly high catalyst activity due to significant characteristics of MgCl<sub>2</sub> such as; similar ionic radii of Mg<sup>2+</sup> and Ti<sup>4+</sup> (0.65 and 0.68 Å, respectively), both belong to the same hexagonal system, highly porous structure, low electronegativity com-

pared to titanium trichloride, and relatively chemical inertness.<sup>8,9</sup> The preparation method of the catalyst is also a key factor for catalyst activity.<sup>10–12</sup>

Despite the superior property of the inorganic oxide supports, they have certain limitations. One of the main concerned problems of these catalysts is that they introduce the metals and chlorides as contaminants into the polyolefin which alters physical properties and stability of the polymer.<sup>13</sup>

To eliminate the above mentioned problems of the inorganic oxide supports, researchers had given much attention to an alternative support to the bare catalyst. One such alternative choice is polymer as support which provides enough flexibility in designing these catalysts by various physico-chemical ways. The polymer-supported catalyst can facilitate the control of particle morphology without involving a pre-polymerization step. In 1993, Ran developed a poly(styrene-divinylbenzene-2%)-supported Ziegler–Natta catalyst for isoprene polymerization with catalytic productivity of 20 kg polyisoprene/g Ti.<sup>14</sup> Ohnishi et al. prepared a novel ethylene-propene-diene-monomer (EPDM)-supported homogeneous Ziegler–Natta catalyst for the production of PE with molecular weight distribution ( $M_w/M_n$ ) = 2.2).<sup>15</sup> Wankes and coworkers developed 2-hydroxyethyl methacrylate functionalized polystyrene (PS)-supported zirconium-based catalyst for ethylene as well as ethylene/1-hexene copolymerization in presence of methylaluminoxane (MAO). The catalyst performed good productivity in ethylene/1-hexene copolymerization (productivity = 5.6 kg /mol Zr h

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Contract grant sponsor: CSIR; contract grant number: 01(2202)/07/EMR-II.

bar) rather than ethylene polymerization (productivity = 0.43 kg PE/mol Zr h bar).<sup>16</sup> In 2011, Jinhua et al. produced PE with nano fiber structure (20–80 nm) from porous poly(styrene-*co*-divinylbenzene-acrylonitrile)-supported Ziegler–Natta catalyst with productivity of 100–200 g PE/ mmol Ti h atm.<sup>17</sup> Recently, Rajesh et al. performed *in-situ* ethylene polymerization with inorganic fillers (MgO, CaCO<sub>3</sub>, and TiO<sub>2</sub>) filled polyethersulfone-supported titanium-based catalyst where, the fillers were pre-treated with cocatalyst (MAO). TiO<sub>2</sub> used as filler showed good productivity due to the high reactivity of Ti-O for ethylene polymerization.<sup>18</sup> In addition, variety of polymeric supports employed in the prior art are poly[propene-*co*-(7-methyl-1, 6-octadien)],<sup>13</sup> poly(ether sulfones),<sup>19</sup> poly(ethylene-*co*-acrylic acid),<sup>20</sup> poly(methyl vinyl ketone),<sup>21</sup> and so on. The main objective of these researches was to develop a catalyst with excellent properties having high activity and high storability.

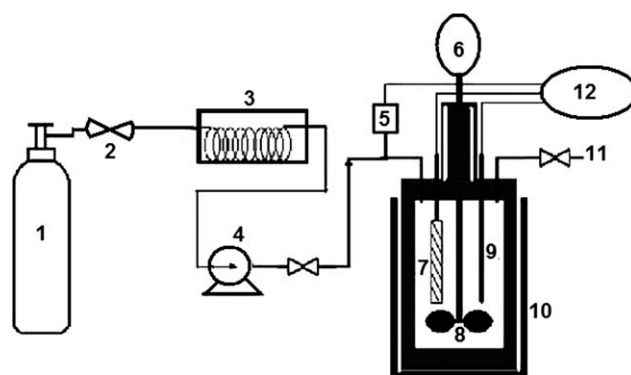
In this article, we have reported the synthesis of novel PS-supported Ziegler–Natta catalyst for ethylene polymerization where PS is synthesized by emulsion polymerization using super critical CO<sub>2</sub> (sc-CO<sub>2</sub>) as a green solvent. The synthesized PS is highly pure rather than other polymers synthesized using different methods where, the polymer needs additional steps for purification to remove byproduct (mainly solvent) from the polymer. The byproduct present in the polymer is responsible for the low activity of the catalyst as well as low storability. It is well known that the role of the polymer support is minimal; the polymer support is considered as an inert matrix holding the catalytic groups. Here PS support is prepared in a green (sc-CO<sub>2</sub>) solvent. Our attempt is to immobilize titanium tetrachloride (TiCl<sub>4</sub>) directly into the polymer matrix in one step without functionalization of the polymer matrix. The present work describes the preparation of PS using sc-CO<sub>2</sub> medium, preparation of polymer-supported catalyst, their characterization, catalytic activity for ethylene polymerization at low temperature (40°C), storability of the catalysts, and polymer morphology.

## EXPERIMENTAL

All manipulations involving air sensitive compounds were performed inside an inert N<sub>2</sub> atmosphere glove box continuously purged with high purity dry nitrogen.

### Material

TiCl<sub>4</sub> and triethylaluminum (TEA) from Aldrich were used without further purification. Styrene (Aldrich, Steinheim, Germany) was deinhibited and purified by washing with 10% NaOH solution, fol-



**Figure 1** Schematic diagram of the apparatus: (1) carbon dioxide cylinder; (2) back pressure valve; (3) refrigeration unit; (4) high pressure liquid pump; (5) back pressure gauge; (6) motor for mechanical stirrer; (7) cooling unit; (8) mechanical stirrer; (9) heating probe; (10) SFE vessel; (11) vent; (12) digital display unit.

lowed by washing with double distilled water. Polydimethylsiloxane (PDMS) (Fluka, Steinheim, Germany), azobisisobutyronitrile (AIBN) (Allied Industries, Mumbai, India) was recrystallized from methanol. Tetrahydrofuran (THF, Ranbaxy, Assam, India) was distilled before use. Carbon dioxide (Rass Chryogenics, Assam, India) (99.99% pure) was used as received. Ethylene (>99.99% purity) was taken from Chemtron Science Lab. Pvt Ltd. (Mumbai, India) and used after passing over a BTS copper catalyst and a 10-Å molecular sieve to remove O<sub>2</sub> and moisture. Hexane and toluene were distilled and kept over molecular sieves before use.

## Procedure

### Synthesis of polystyrene

The polymerization was performed in a 60 mL, high pressure reactor (SFE-System, Reaction Eng. Inc. Korea) equipped with a magnetically coupled overhead stirrer. The schematic diagram of the apparatus is shown in Figure 1.

For polymerization of styrene initially, reactor was charged with PDMS (0.5 g) stabilizer. Then AIBN (0.1 g) and styrene (10 mL) were added into the reactor and mixed thoroughly. The reactor was pressurized by filling with CO<sub>2</sub> to 7 MPa, and heated to the desired reaction temperature (75°C). With the increase in temperature, the pressure gradually increases. Once the reaction temperature was reached, the desired pressure (13.79–17.93 MPa) was maintained by venting the CO<sub>2</sub>. The reaction was allowed to proceed for 8 h at temperature 75°C. At the end, the reactor was allowed to cool down to room temperature. The pressure was then slowly released and at atmospheric pressure the polymeric product was recovered from the reactor as a fine white powder followed by washing and vacuum drying.<sup>22</sup>

TABLE I  
Experimental Condition for Synthesis of PS-Supported Titanium-Based Catalysts

| Entry                          | Cat1                        | Cat2                        | Cat3                        |
|--------------------------------|-----------------------------|-----------------------------|-----------------------------|
| PS(g)                          | 1.5                         | 1.5                         | 1.5                         |
| TiCl <sub>4</sub> (g)          | 0.964                       | 2.892                       | 4.82                        |
| TiCl <sub>4</sub> /PS wt ratio | 0.642                       | 1.92                        | 3.21                        |
| Stoichiometry composition (g)  | PS(1.5) : Ti(0.2) : Cl(0.7) | PS(1.5) : Ti(0.7) : Cl(2.1) | PS(1.5) : Ti(1.2) : Cl(3.5) |
| Physical nature                | Orange powder               | Orange powder               | Orange powder               |

#### Preparation of PS-supported heterogeneous catalyst

PS-supported Ziegler catalysts were prepared using PS as a starting material. The delocalized  $\pi$ -electrons of the benzenoid moiety (electron donor) acted as a reactive site for reaction with TiCl<sub>4</sub> (electron acceptor). Thus three catalysts of PS-TiCl<sub>4</sub> were synthesized by varying the TiCl<sub>4</sub>/PS weight ratio (Table I).

In an inert atmosphere inside the glove box, 1.5 g of PS were dispersed in 45 mL of dry, oxygen-free hexane at 25°C under nitrogen in a 100-mL round-bottom flask with stirring. With a gas tight syringe prescribed amount of TiCl<sub>4</sub> solution in toluene was added dropwise with constant stirring. After the addition was complete, the mixture was kept stirred for additional 6 h at room temperature. The resulting solid product was then filtered and rinsed with ample amounts of dry toluene to remove the unreacted TiCl<sub>4</sub> and dried under reduced pressure at 50°C for 24 h. The dried products were subjected to titanium estimation following colorimetric method using UV-visible spectroscopy.<sup>14,23</sup>

#### Polymerization of ethylene using polymer-supported titanium-based catalyst in slurry phase

All the polymerizations were carried out in a 150 mL steel-jacket high pressure autoclave reactor in the slurry phase. The reactor was equipped with a magnetic stirrer, an external water jacket for temperature control, a septum inlet, and a regulated supply of dry nitrogen and ethylene. Before carrying out the reaction, the reactor was heated at approximately 115°C for 2 h. Also all the glass wares were heated to 120°C for 3 h at oven and subsequently allowed to cool under nitrogen atmosphere.

Ethylene polymerization was performed in the presence of TEA as a cocatalyst to evaluate the catalyst activity of supported catalyst. After depletion of all moisture and oxygen, 100 mL dry hexane was added to the reactor under nitrogen pressure. The solution was allowed to be saturated with ethylene followed by addition of TEA (10%, v/v; Al/Ti mole ratio = 250) for alkylation. Finally, the catalyst (0.04 g) was injected into the reactor to start the polymerization at 40°C and atmospheric pressure. The flow of ethylene was maintained during the 60 min of poly-

merization to keep the saturated concentration of ethylene at atmospheric pressure. After the polymerization, the reaction was quenched with ethanol containing 20 vol % of conc. HCl and subsequently the untreated gases were slowly released. The precipitate polymer was filtered, washed with methanol, and dried in vacuum at 70°C.

By following the same procedure, ethylene polymerization is carried out with the other two catalysts maintaining specific condition (Table IV).

#### Characterization

##### UV-visible spectra

The titanium content of the synthesized catalysts was determined by colorimetric method. For determination of titanium content, the polymer-supported catalysts were dissolved in an acidic media followed by dilution with double distilled water to 100 mL. The diluted solution was reacted with H<sub>2</sub>O<sub>2</sub> to form peroxotitanium complex [TiO(H<sub>2</sub>O<sub>2</sub>)]. UV-visible spectra of the resultant solution of peroxotitanium complexes were recorded on a Hitachi U-2001UV-visible spectrophotometer. The peak intensity at 410 nm was used to quantify the titanium content.

##### pH determination of the polymer-supported TiCl<sub>4</sub> complex

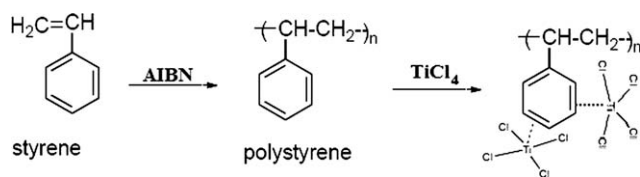
The catalyst was hydrolyzed in 60% acetone solution in water at room temperature. The pH of the resultant solution was measured by a standard pH (Orion multiparameter kit).

##### Infrared spectra

The infrared (IR) spectra of the catalysts were recorded in Nicolet Impact-410 IR spectrometer in KBr medium at room temperature in the region 4000–450 cm<sup>-1</sup>.

##### Scanning electron microscopy and energy dispersive X-ray detector (SEM-EDX)

The morphology of the polymer particles and energy dispersion spectroscopic analysis of catalysts was examined by using the JEOL-JSM-6390LV SEM



**Scheme 1** Synthetic scheme of PS and PS- $\text{TiCl}_4$  complex.

attached with EDX. Samples were coated with platinum to a thickness of 200 Å. The voltage and working distance was varied during the measurements. The EDX instrument was operated at 20 kV which was conducted on the same specimen in an effort to obtain semi-quantitative compositional information.

#### Thermogravimetric analysis

Thermogravimetric analysis (TGA) of pure polymer and polymer-supported  $\text{TiCl}_4$  catalysts was studied in a Shimadzu TGA-50 Thermal analyzer over a temperature range of 30–600°C with the heating rate 5 °C/min under  $\text{N}_2$  atmosphere.

#### Gel permeation chromatography

Molecular weight of the PS and PE was determined by gel permeation chromatography (GPC, Waters, Taunton, USA) using tetrahydrofuran (THF)/1,2,4-trichlorobenzene as a mobile phase.

#### Differential scanning calorimetry

The melting point of polymers was measured by differential scanning calorimetry (DSC, Model DSC-60, Shimadzu) at a heating rate of 5 °C/min under the nitrogen flow rate of 30 mL/min from 0 to 400°C.

#### X-Ray diffraction analysis

Powder X-ray diffraction (XRD) data were collected on a Rigaku Miniflex X-ray diffractometer with  $\text{Cu K}_\alpha$  radiation ( $\lambda = 0.15418$  nm) at 30 kV and 15 mA using a scanning rate of 0.05°/s in  $2\theta$  ranges from 10° to 70°.

## RESULTS AND DISCUSSION

### Characterization of PS and PS-supported titanium-based catalysts

#### Synthesis of polystyrene and PS- $\text{TiCl}_4$ catalysts

PS is prepared via a two step method in  $\text{sc-CO}_2$ ; initially, monomer and initiator form microemulsion under room temperature and vigorous stirring condition. PDMS which act as a stabilizer covers the micro droplet of the monomer and impart stability to the microemulsion. In the second step, when the

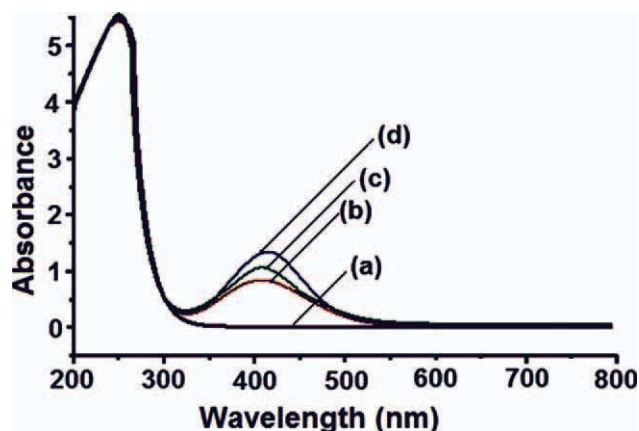
temperature reaches 75°C the initiator decomposes and initiates the polymerization. To carry out the reaction,  $\text{CO}_2$  is used as a reaction medium where monomer droplets are dispersed in  $\text{sc-CO}_2$  and allowed to polymerize. After termination of the reaction, the polymer powders are collected by slowly depressurizing and cooling the reactor. The molecular weight of the synthesized PS, is  $M_n = 35,542$  g/mol and the polydispersity,  $M_w/M_n = 1.45$ .

The polymer-supported  $\text{TiCl}_4$  catalyst was prepared by complexation of PS with  $\text{TiCl}_4$ . The complex formation takes place via the formation of a coordination bond between the  $\text{TiCl}_4$  and the PS. Since  $\text{TiCl}_4$  ( $d^0$ ) has the vacant d-orbital so it has the ability to accept the  $\pi$  electron donated from the electron rich PS moiety leading to a  $\text{TiCl}_4$ -PS complex. The probable way of complex formation is shown in Scheme 1. The donation of electron from PS moiety to Ti stabilizes coordination of monomer and subsequently facilitates monomer insertion.<sup>24,25</sup>

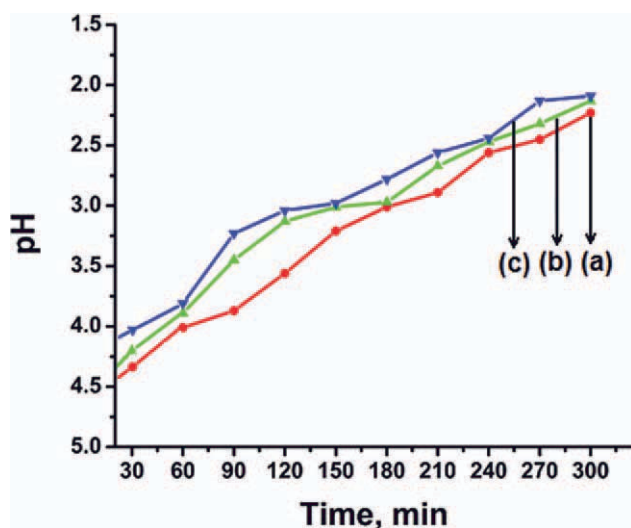
#### UV-visible spectroscopy

The UV-visible spectra of the solution of a pristine polymer and its complex with  $\text{TiCl}_4$  are shown in Figure 2. As expected, the Ziegler-Natta catalyst does not show any absorption band in the UV-visible region. However, to confirm the presence of titanium in the hybrid catalysts (Cat1–Cat3), we have digested it with 20% conc.  $\text{H}_2\text{SO}_4$  and subsequently extracted the titanium from the complex to the solution by forming a peroxotitanium complex with 30% (w/v)  $\text{H}_2\text{O}_2$ .

The broad peak observed at 410 nm [Fig. 2(b)] is attributed to  $p_\pi \rightarrow d_\pi$  transition that arises due to the transition of lone pair of electrons on oxygen to the vacant d-orbital of  $\text{Ti}^{4+}$ . The presence of this broad spectrum confirms the formation of peroxotitanium complex and the presence of Ti in the catalyst.



**Figure 2** UV-visible spectra of pristine (a) PS, (b) Cat1, (c) Cat2, and (d) Cat3. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

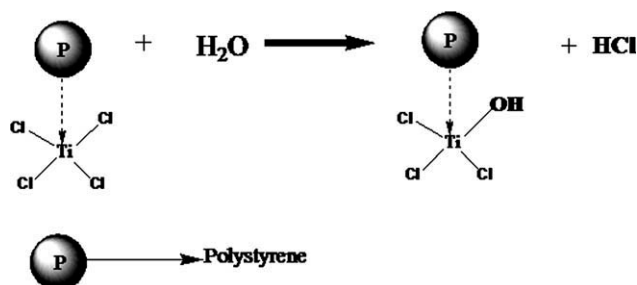


**Figure 3** Change of the pH of 50 mL acetone–water solution (60%) containing 1 g PS-TiCl<sub>4</sub> catalyst with time; (a) Cat1, (b) Cat2, and (c) Cat3. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Interestingly, on increasing the amount of TiCl<sub>4</sub>, the absorption peak intensities also increase gradually [Fig. 2(c,d)] indicating the successful incorporation of TiCl<sub>4</sub> into the polymer matrix. The peak intensity at 410 nm is used to quantify the titanium content by colorimetric method. The wt % titanium of the modified catalysts (Cat1–Cat3) is found to be in the range of 0.9–4.6 (Table IV) followed by colorimetric method. But in case of pristine polymer [Fig. 2(a)] only one broad peak is observed at around 280 nm due to the  $n-\pi^*$  transition of the phenyl ring of PS.

Acidity of the solution obtained on hydrolysis of PS-TiCl<sub>4</sub> catalysts

The pH of an acetone–water solution (60%) containing PS-supported TiCl<sub>4</sub> complex beads are shown in Figure 3(a–c). From Figure 3(a) it is observed that the acidity due to hydrolysis of the Cat1 gradually increases. This is due to the release of HCl to the solution after reaction of TiCl<sub>4</sub> incorporated in PS with water (Scheme 2). Thus, it is clear that some amount of TiCl<sub>4</sub> is present in the complex. Similar trend is



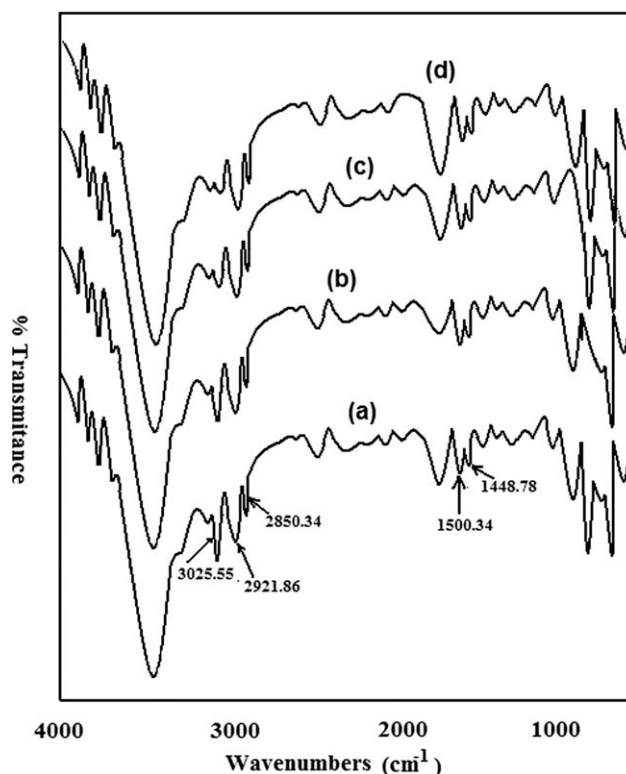
**Scheme 2** Probable way of hydrolysis of PS-TiCl<sub>4</sub> catalyst.

also observed in case of other two catalysts (Cat2 and Cat 3) with slight more pH, which reveals the higher amount of TiCl<sub>4</sub> anchored into the polymer matrix. On the other hand, the pristine PS shows pH of about 7.4 in acetone–water solution (60%).

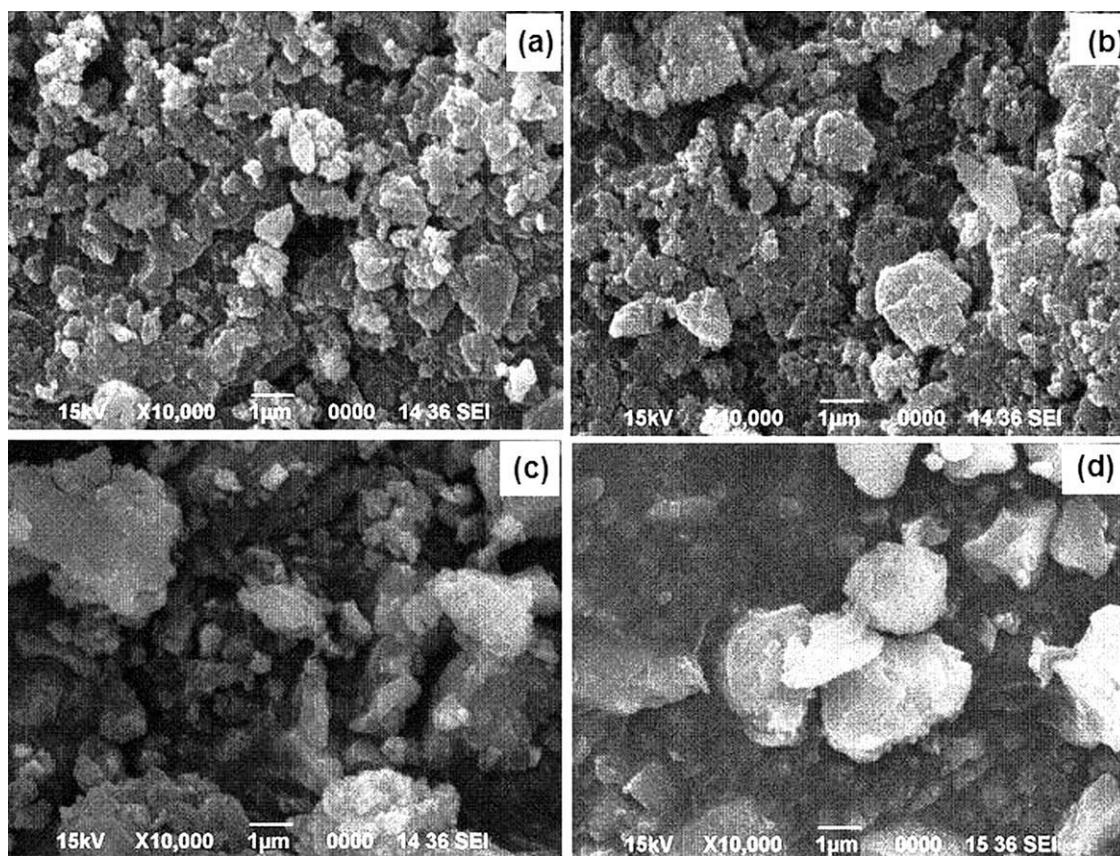
FTIR studies of PS and PS-TiCl<sub>4</sub> catalysts

Fourier transformed-infrared spectroscopy (FTIR) spectra of PS and PS-TiCl<sub>4</sub> catalysts are shown in Figure 4(a–d). The IR bands of PS are clearly observed; the broad band at about 3450 cm<sup>-1</sup> is due to the peak overlap of C–H and =C–H of PS and O–H of the adsorbed H<sub>2</sub>O. The peak near 3025 cm<sup>-1</sup> is characteristic of =C–H stretching modes for monosubstituted benzene ring, while those at 2923 and 2850 cm<sup>-1</sup> are assigned to the C–H stretching modes for the –CH– and –CH<sub>2</sub>– groups on the alkyl chain of the polymer. The bands in the range 1450–1598 cm<sup>-1</sup> are assigned to the characteristic skeleton vibration of the ring C–H and alkyl –CH–, –CH<sub>2</sub>– bending modes. The peak obtained at about 748 and 697 cm<sup>-1</sup> are related to single substrate of the phenyl ring.

On heterogenation of TiCl<sub>4</sub> on the PS, the color of the polymers changes from white to orange. Comparing the IR spectra of PS and PS-TiCl<sub>4</sub> catalyst, peak intensity of 3025 cm<sup>-1</sup> interestingly decreases, indicating a reduction in the electron density on the



**Figure 4** Infrared spectrums of (a) PS, (b) Cat1, (c) Cat2, and (d) Cat3.



**Figure 5** SEM micrographs of the (a) PS, (b) Cat1, (c) Cat2, and (d) Cat3.

C=C  $\pi$  conjugated bond. This is due to the donation of electron density from  $\pi$  bond to the vacant d orbital of Ti in  $\text{TiCl}_4$ . This lowering of stretching frequency continued to become more dramatic as the amount of  $\text{TiCl}_4$  loading into the polymer chain increases (Cat1–Cat3).

#### SEM and EDX studies

SEM-EDX technique has great potential as an effective tool to observe the surface morphological information of the polymer and the distribution of the titanium species on the polymer support. The SEM micrographs of the pristine polymer and the synthesized PS- $\text{TiCl}_4$  catalysts are given in the Figure 5(a–d), respectively. The morphology of the pure polymer and the prepared catalysts is found to be slightly different. From the Figure 5(a), it can be seen that the pristine polymer exhibit randomly aggregate irregular shape and size, namely non-spherical with an average diameter of 2  $\mu\text{m}$ . In case of catalysts after incorporation of  $\text{TiCl}_4$  on the polymer matrix, it is observed that the particle size becomes slightly larger than the pristine one. Moreover the surface becomes slender smooth. This may be due to interaction of the aromatic  $\pi$  electrons of the PS with  $\text{TiCl}_4$ . The observed increase in particle diameter of

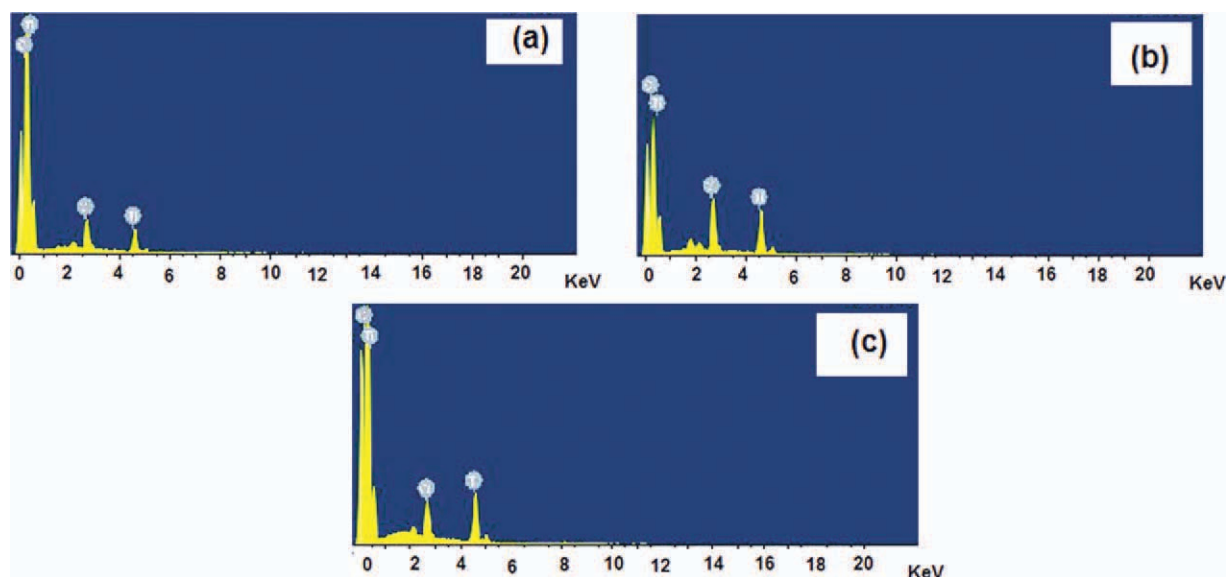
the catalyst particle could be a further evidence of an effective anchoring of  $\text{TiCl}_4$  with the polymer.

The quantitative elemental analysis of PS-supported  $\text{TiCl}_4$  catalysts was determined with EDX analyzer at room temperature. Figure 6(a–c) shows EDX spectra of the synthesized polymer-supported catalyst. Presence of titanium and chlorine in the polymer matrix confirms beyond any reasonable doubt that  $\text{TiCl}_4$  is successfully incorporated with PS matrix. With the increase in amount of  $\text{TiCl}_4$  in the polymer matrix, Ti content in the supported catalysts also increases and reaches to maximum of 66.7 wt % as measured by EDX (Table II). It is worth mentioning that EDX analyzer quantifies only the element present in the uttermost catalyst surface. The result shows that the titanium is exclusively present in the surface of the catalysts as expected.

It is clear that adjusting the relative amount of PS and  $\text{TiCl}_4$ , the amount of Ti loading onto the polymeric species can be controlled.

#### XRD

XRD pattern of the pristine PS and the synthesized PS-supported  $\text{TiCl}_4$  catalysts are shown in Figure 7(a–d). In the range of 20–35° diffraction angles, a wide reflection peak is observed for pure PS due to



**Figure 6** EDX patterns of the (a) Cat1, (b) Cat2, and (c) Cat3. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

the crystalline nature of PS. But in case of Cat1 after addition of TiCl<sub>4</sub> into the polymer matrix, the intensity of characteristic reflection peak has been considerably diminished without altering the peak position, indicating the loss of crystallinity of the pristine polymer. With the increased addition of TiCl<sub>4</sub> the intensity of the crystalline peak is drastically reduced and become totally amorphous in nature. It is thus clear that with subsequent incorporation of TiCl<sub>4</sub>, the peak intensity of crystallinity decreases gradually. To our knowledge, the decrease in peak intensity occurred because of the accommodation of TiCl<sub>4</sub> molecules onto the PS which combine the polymer chain.

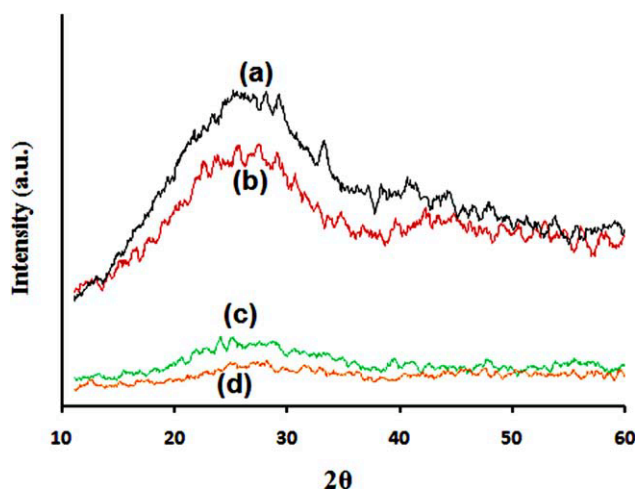
#### TGA

The thermal behavior of the pure polymer and the polymer-supported catalysts has been examined by TGA and the TGA curves are shown in Figure 8(a–d). The characteristic degradation temperature of the polymer and catalysts are presented in Table III.

The initial decomposition temperature of the pristine PS is occurring in the range of 250–300°C. The major degradation of the polymer chain occurs in the range of 350–450°C and the loss is related to breaking of main chain and side group of PS. But in

case of TiCl<sub>4</sub> incorporated PS catalyst, the weight loss starts at 180°C with a little deviation from that of pristine PS. This weight loss could be assigned to the volatilization of residual solvent, HCl, and absorbed water. All the degradation temperatures (1st, 2nd, and 3rd) gradually decrease with the incorporation of TiCl<sub>4</sub> into the polymer matrix. This is mainly due to loss of crystallinity of PS by incorporation of TiCl<sub>4</sub>.

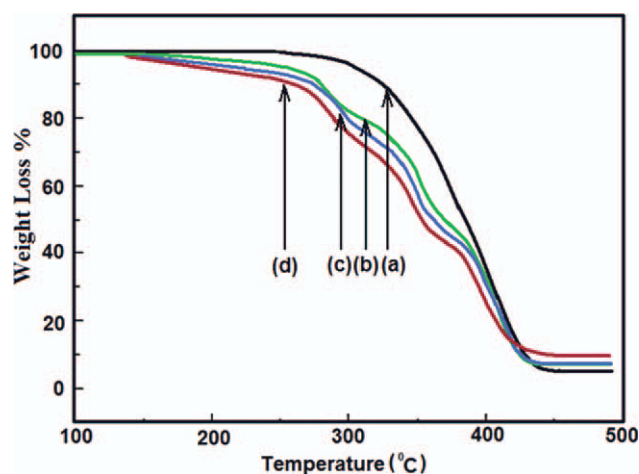
TG analyses show that TiCl<sub>4</sub>-polymer catalysts are stable up to 170–200°C (depending on percent of TiCl<sub>4</sub> loading). Since olefin polymerization with conventional Ziegler–Natta catalyst system is carried out at 60–80°C; so it may be inferred that these newly synthesized catalysts are sufficiently



**Figure 7** Powder X-ray diffraction patterns for (a) PS, (b) Cat1, (c) Cat2, and (d) Cat3. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**TABLE II**  
Surface Composition of the PS-TiCl<sub>4</sub> Catalysts

| Entry | Ti (wt %) | Cl (wt %) |
|-------|-----------|-----------|
| Cat1  | 51.35     | 48.65     |
| Cat2  | 58.63     | 41.37     |
| Cat3  | 66.70     | 33.30     |



**Figure 8** TGA curves of (a) PS, (b) Cat1, (c) Cat2, and (d) Cat3. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

thermally stable to be applied as supports with Ziegler–Natta catalyst for olefin polymerization.

### Catalytic activity of PS-TiCl<sub>4</sub> catalyst on ethylene polymerization

Polymerization of ethylene is conducted with PS-supported Ziegler–Natta catalyst in the presence of TEA in hexane at 40°C and atmospheric pressure, which is rather mild than the typical industrial condition. The polymerization of ethylene proceeds in a heterogeneous system, because the catalysts prepared from PS were insoluble in the solvent (hexane) used for ethylene polymerization. Due to the heterogeneous nature of the catalysts, the polymerization started at the surface of the PS-supported catalyst.<sup>13</sup> It is well known that the cocatalyst TEA reduced Ti<sup>4+</sup> to Ti<sup>3+</sup> in TiCl<sub>4</sub> and formed Ti–C bond which is considerably active for ethylene polymerization.<sup>11</sup>

The catalytic activity of the three catalysts (Cat1, Cat2, and Cat3) is evaluated for polymerization of ethylene under identical condition. The activity is determined in terms of weight of PE produced per gram of Ti used in 1 h polymerization. All the catalyst shows the productivity in the range of 2376–3720 g of PE/g of Ti/h (Table IV). The activity of

**TABLE III**  
Degradation (deg) Temperatures of the PS and PS-TiCl<sub>4</sub> Catalysts

| Entry | Degradation temperature(°C) |         |         |
|-------|-----------------------------|---------|---------|
|       | 1st deg                     | 2nd deg | 3rd deg |
| PS    | 250                         | 350     | 450     |
| Cat1  | 200                         | 300     | 380     |
| Cat2  | 180                         | 290     | 360     |
| Cat3  | 170                         | 280     | 350     |

**TABLE IV**  
Polymerization Condition and Activity of Three Catalysts in Ethylene Polymerization

| Entry  | Cat1  | Cat2  | Cat3  |
|--|-------|-------|-------|
| Ti wt % (UV-visible)                               | 0.9   | 2.1   | 4.6   |
| Catalyst amount (g)                                | 0.04  | 0.04  | 0.04  |
| Al/Ti mole ratio                                   | 250   | 250   | 250   |
| Ethylene pressure                                  | 1 atm | 1 atm | 1 atm |
| Reaction temperature (°C)                          | 40    | 40    | 40    |
| Solvent (mL)                                       | 100   | 100   | 100   |
| Polymerization time (h)                            | 1     | 1     | 1     |
| Productivity<br>(g of polyethylene/g of Ti/ h)     | 2376  | 3720  | 2770  |
| Wt % of the polymer<br>support in the resulting PE | 3.9   | 2.3   | 2.4   |

the catalyst Cat2 which have Ti content of 2.1 wt % is higher than that of Cat1 due to the more amount of Ti in to polymer matrix which increases the active site for ethylene polymerization after alkylation. But after a certain limit of Ti, the activity gradually decreases (Cat3). This is due to the fact that if more is the amount of TiCl<sub>4</sub> anchored into the polymer matrix, more is the probability of formation of TiCl<sub>4</sub> clusters which reduces the active sites.

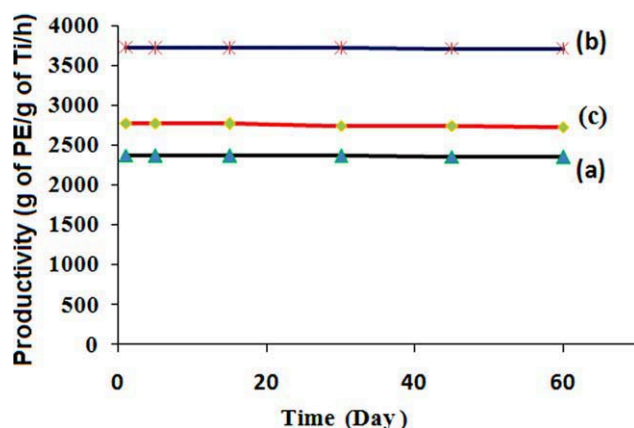
### Stability of the supported catalysts

The important criterion of the supported catalysts is that the immobilized Ti complex after alkylation with TEA should not be removed from the support during polymerization. To study the leaching property of the catalysts the following experiments were conducted. In a 250-mL three necked round bottom flask, 0.04 g Cat1 was dispersed in dry hexane in an inert nitrogen atmosphere. Calculated amount of TEA (Al/Ti = 250) was injected into the solution with a gas tight syringe. After vigorously stirring at 40°C for about 2 h, the mixture was filtered in dry nitrogen atmosphere. The titanium content of the filtrate was estimated following colorimetric method using UV–visible spectroscopy as mentioned above. The absence of trace amount of titanium reveals no leaching during alkylation with TEA. The same experiment was performed for the other two catalysts (Cat2 and Cat3) and found no leaching of Ti. It is confirmed that Ti complex is anchored firmly on PS matrix.

### Effect of catalytic activity of the catalysts with storage time

The major snag arises in storing and handling of TiCl<sub>4</sub> and Et<sub>3</sub>Al since they are highly moisture sensitive and corrosive in nature. But interestingly, synthesized PS-supported Ziegler–Natta catalyst can be stored easily in a stopper vessel at nitrogen atmosphere. In order to evaluate the catalytic activity vs.





**Figure 9** Catalytic productivity with storage time (a) Cat1, (b) Cat2, and (c) Cat3. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

storability of the catalysts, ethylene polymerization is conducted by maintaining the aforesaid specific condition. It is observed that the synthesized catalysts (Cat1–Cat3) retain their catalytic activity for ethylene polymerization upto 60 days (Fig. 9).

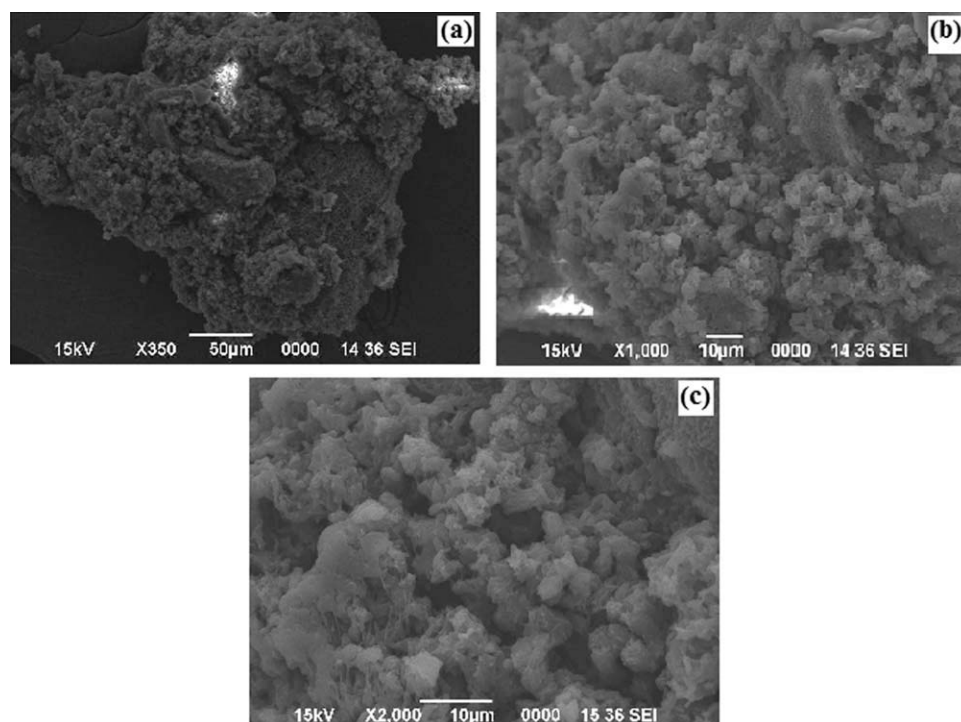
#### Characterization of the obtained PE

The SEM of PE is shown in Figure 10. It is observed that at lower magnification of  $\times 350$ , the polymer seems to be porous granules-like structure but at higher magnification ( $\times 2000$ ), the polymer granules

seem to be porous fiber like. The sizes of the PE granules were much larger than that of the polymer-supported catalysts. This might be due to the fact that during polymerization, the resulting polymer particles pack together to form well-built PE granules where, the catalyst particles act as a template for growth of the polymer particles.

The molecular weight of the PE was measured by GPC and the data are listed in Table V. It is observed that the PE exhibited number-average molecular weights ( $M_n$ s) in the range of 24,900–31,400 g/mol with broad molecular weight distribution of 9.1–10.3. This phenomenon indicates that the catalyst contains more than one type of active sites since the catalysts are heterogeneous in nature so it is very challenging to produce single-site catalyst which is responsible for producing narrow polydispersity ( $PDI = < 2$ ) PE. The melting point of the PE is found to be 134.5–135.7°C (Table V). The high melting point indicates the less branched structure of PE.

The rheological properties of the resulting PE were studied by melt flow index (MFI) and the data are provided in Table V. It is observed that MFI of the PE decreases with increase in molecular weight of the resulting PE. The bulk density of the ensuing PE increases with increasing polymerization activity (Table V). However, the bulk density of the PE is relatively low (0.19–0.28 g/cm<sup>3</sup>, runs Cat1, Cat2, Cat3) which is due to the lower ethylene pressure. It has been found that 2.3–3.9 wt % of polymer support has been incorporated (Table IV) in the



**Figure 10** SEM images PE synthesized from PS-TiCl<sub>4</sub>-supported titanium catalyst (Cat2) collected at magnification of (a) 350 $\times$  (b) 1000 $\times$ , and (c) 2000 $\times$

TABLE V  
Characterization of Polyethylene Synthesized by PS-Supported Titanium Catalysts

| Entry | $M_n(\text{GPC})$ | $M_w(\text{GPC})$ | PDI  | $T_m$ (°C) | MFI (g/10 min) | Bulk density (g/cm <sup>3</sup> ) |
|-------|-------------------|-------------------|------|------------|----------------|-----------------------------------|
| Cat1  | 25,700            | 247,400           | 9.6  | 135.7      | 1.86           | 0.19                              |
| Cat2  | 31,400            | 286,800           | 9.1  | 134.5      | 1.23           | 0.28                              |
| Cat3  | 24,900            | 256,500           | 10.3 | 134.8      | 1.67           | 0.23                              |

MFI (230°C/2.16 kg)

synthesized PE which may have negligible effect on the properties of the synthesized PE.

### CONCLUSION

In summary, we have successfully synthesized PS-supported  $\text{TiCl}_4$  catalyst in hexane medium. The FTIR spectral analysis showed the interaction of  $\text{TiCl}_4$  with the PS moiety. It is found that the Ti content in the polymer matrix gradually increases (0.9–4.6 wt %) with the increase in amount of  $\text{TiCl}_4$ . PS lost its crystallinity with the incorporation of  $\text{TiCl}_4$  and becomes completely amorphous in nature. PS- $\text{TiCl}_4$  catalysts are stable upto 150–180°C (depending on percent of  $\text{TiCl}_4$  loading).

PS-supported Ziegler–Natta catalysts after alkylation with TEA are used for ethylene polymerization in slurry process. These catalysts performed different productivity (2376–3720 g of PE/g of Ti/h) with different composition (0.9–4.6 wt %) of titanium in polymer matrix. Catalyst with 2.1 wt % of titanium showed maximum activity, which gives clear indication that not only quantity of titanium but also the uniform distribution of Ti in the polymer matrix is a governing factor for catalytic activity. The PS- $\text{TiCl}_4$  catalysts retained their catalytic activity upto 60 days when stored in an inert atmosphere stopper vessel.

However, these catalysts show low activity in comparison with commercial  $\text{MgCl}_2$ -supported Ziegler–Natta catalyst. Further study is required to improve the catalytic activity.

Authors are also thankful to Reliance Industries Limited (RIL), Hajira, India for helping them to analyze the catalytic activity of the catalyst.

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