

# Preparation and Characterization of Ceria Nanoparticles Supported on Poly(4-vinyl pyridine-co-divinyl benzene)

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**ABSTRACT:** Formation of ceria nanoparticles in 2% divinyl benzene (dvb) crosslinked 4-vinyl pyridine (4vp) polymer [poly(4vp-co-dvb)] microspheres was investigated. The polymer was prepared by free radical suspension polymerization method. Poly(4vp-co-dvb)/ceria nanocomposites were prepared by reacting  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  and NaOH in the presence of poly(4vp-co-dvb) at room temperature in aqueous media. The mole ratio of the metal to polymer was varied from 2.5 to 10% with an increment of 2.5. The polymer and nanocomposites were characterized by various spectrochemical methods. The coordination of nitrogen at-

oms of the polymer with Ce(IV) of ceria ( $\text{CeO}_2$ ) has been confirmed from X-ray photoelectron spectroscopy (XPS). The method has yielded ceria nanoparticles in an average size of 15 nm according to transmission electron microscopy. Differential scanning calorimetry, thermogravimetric analysis, X-ray diffractometry and XPS analysis with respect to mole percentage of ceria in the composite are discussed. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3439–3445, 2006

**Key words:** vinyl pyridine copolymer; ceria; nanocomposite; X-ray diffraction

## INTRODUCTION

Incorporation of inorganic materials on nanoscale into organic polymers leads to the generation of nanostructured materials, with improved electrical, mechanical, and optical properties, opening up diverse applications as catalysts, electronic or photonic devices, sensors, etc. Therefore, nanostructured metal-polymer and metal oxide-polymer composites have been the subject of great interest to researchers. These composites can be prepared by a heterogeneous method, with the polymer powder suspended in nanosized metal solutions, or homogeneous method, where the solutions of metal nanoparticles and polymer are mixed together. An excellent method to achieve good dispersion of metal particles is preparation of metal nanoparticles in situ on the polymer matrix.

Polymers containing nitrogen basic groups can be used in the preparation of such nanocomposites, because of the capacity of the nitrogen atom to coordinate with the metals. Superparamagnetic nanoparticles of cobalt oxide, iron oxide, and nickel oxide were prepared in a poly(vinyl pyridine) matrix, with an average size of 50–100 nm, by Ramos et al., following homogeneous and heterogeneous methods.<sup>1</sup> A similar procedure was reported for the preparation of magnetic nanocomposites of poly(4-vinyl pyridine) and

iron oxides by Millan and Palacio, where the reaction of polymer with the metal is proposed to be through surface reaction mechanism.<sup>2</sup> Colloidal gold nanoparticles were produced on the surface of poly(2-vinyl pyridine) film by adsorption from a dilute aqueous suspension.<sup>3</sup> Palladium(II) nanoparticles were selectively incorporated into the microdomain spaces of polyisoprene-*b*-poly(2-vinyl pyridine) via in situ reduction of metal ions.<sup>4</sup> Malynych et al. have reported that vinyl pyridine polymers can immobilize metal and nonmetal nanoparticles to produce different single and multilayered assemblies.<sup>5</sup> Poly(4-vinyl pyridine) resin quarternized with 2-chloroacetamide was used for selective mercury extraction by Sonmez et al.<sup>6</sup> Reports on the production of ceria nanoparticles, which are intensively used in metallurgy, catalysis, function ceramics etc., supported on  $\text{Al}_2\text{O}_3$ ,<sup>7</sup>  $\text{SiO}_2$ ,<sup>8</sup> activated carbon,<sup>9</sup> and carbon nanotubes<sup>10</sup> are known. However, in situ preparation of ceria nanoparticles supported on polymers is found to be very limited. Masui et al. has prepared cerium(IV) oxide ultrafine particles dispersed in Nylon-11 film, using the thermal relaxation technique known as relaxative autooxidation (RAD) process.<sup>11</sup>

In the present work, we report the production of ceria nanoparticles in situ on poly(4-vinyl pyridine-co-divinyl benzene) (poly(4vp-co-dvb)) by reacting  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  and NaOH in the presence of dispersed polymer at room temperature in aqueous media. Normally, a hydrothermal treatment is used for generation of nanosized metal oxide, phosphate, sulfide etc.<sup>12–14</sup> The effect of metal to polymer ratio on the properties

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of the composites in comparison to the pure copolymer was studied. The prepared nanocomposites were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and ultraviolet-visible spectroscopy (UV-vis). The morphological and thermal stabilities as a function of concentration of ceria nanoparticles in the composites are discussed.

## EXPERIMENTAL

### Materials

4vp, dvb, *tert*-amylperoxy 2-ethyl hexane carbonate (Luperox 101), and 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (Lupersol TAEC) were purchased from Aldrich Chemicals, USA. Poly(vinyl pyrrolidone) (K-30) (PVP), cerium trichloride heptahydrate ( $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ ), sodium hydroxide (NaOH), and reagent grade methanol were procured from SD Fine Chemicals, India. 4vp was purified by distillation under vacuum prior to use, while the others were used as obtained without further purification.

### Synthesis of poly(4vp-co-dvb)

The copolymer was prepared by suspension copolymerization method, using 4vp and 2 mol % dvb (on 4vp). Into a four-necked resin kettle, fitted with a half-moon Teflon blade agitator, nitrogen purge adapter, and a reflux condenser containing 2.5% (by weight) PVP distilled aqueous solution, a mixture of 4vp, dvb, and 2% Lupersol TAEC initiator (w/w on monomers) was added dropwise while operating the blade agitator at 650 rpm at room temperature. The nitrogen purge was continued throughout the reaction. The bath temperature is raised to 89°C and maintained for an hour before increasing further to 100°C. The second initiator, 1% Luperox 101 (w/w based on monomers) is added to the reaction mixture. The reaction was allowed to proceed for 5 h, with continuous agitation. The copolymer is filtered and washed thoroughly with hot water to remove the water-soluble PVP followed by methanol, to remove the linear polymer and traces of unreacted monomers. The off-white colored copolymer microspheres were dried overnight under vacuum at 65°C and stored.

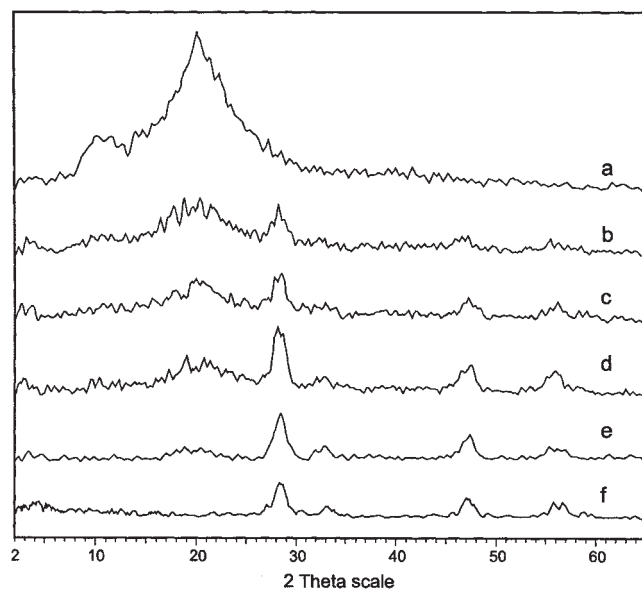
### In situ preparation of $\text{CeO}_2$ nanoparticles on poly(4vp-co-dvb)

One gram of the poly(4vp-co-dvb) was dispersed in 100 mL of distilled water, whose pH is adjusted to 10 by addition of 0.1M NaOH. The calculated mole percentages (2.5–10 mol %) of  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  was added to the polymer dispersion. A shift in the pH toward acidic is balanced by constant addition of 0.1M NaOH to maintain pH 10, until a color change to reddish

orange is noticed which turns yellow after 24 h. The reaction mixture is left for a total time period of 72 h under constant stirring for complete metal-polymer bond formation. The composite of ceria nanoparticles supported on the copolymer was then filtered and washed thoroughly with distilled water until neutral. The ceria supported polymer thus obtained is dried under vacuum at 100°C.

### Nanocomposite characterization

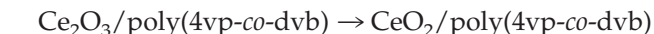
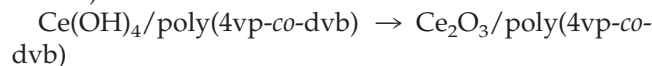
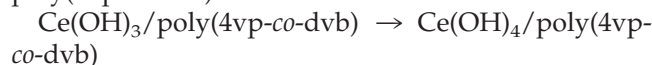
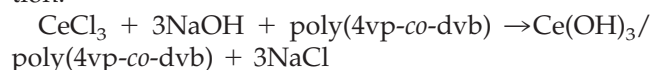
The size and morphology of the nanosized ceria particles supported on the polymer were investigated by scanning electron microscope (SEM) and XRD analysis, and the size of metal particles was measured by transmission electron microscope (TEM). A broad absorbance band for the composites, covering the band for pyridine ring of the pure copolymer, at 230 nm and ceria nanoparticles at 365 nm was observed in UV-vis spectroscopy. Identification of the free N1s peak from the copolymer and the metal-coordinated nitrogen peak of the nanocomposites and the oxidation state of cerium was done using XPS. The effect of metal content on the glass transition temperature of the composites was studied by differential scanning calorimeter (DSC). TEM observation was conducted on a Technai-12 (model) instrument and observed at an acceleration voltage of 100 kV. To obtain the microscopic images of cerium oxide nanoparticles, a drop of the dilute dispersion was deposited by slow evaporation on a copper grid covered with a formal carbon membrane. SEM studies were performed on Hitachi 5S 520 SEM under high vacuum, 0.1 Torr, and high voltage of 1.2 kV, by mounting the gold-coated samples on aluminum stubs, with double-sided adhesive tape. XRD analysis was done on a Rigaku Dmax- $\gamma_A$  XRD using Cu  $K\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). XPS measurements were made on a KRATOS AXIS 165 X-ray Photoelectron Spectrometer instrument using monochromatic Al  $K\alpha$  radiation. Survey scan (0–1000 eV binding energy range) was used to identify the surface elemental compositions of MCPUs. The X-ray gun was operated at 15 kV and 20 mA. Survey and high-resolution spectra were collected using 80 and 40 eV pass energy respectively. The pressure in the analyzer chamber was  $\sim 1.33 \times 10^{-6}$  Pa. UV-vis spectra were measured on a Cintra10e-UV Spectrophotometer. Calorimetric analysis was carried out on 27 HP DSC Mettler Toledo instrument. Thermogravimetric analysis (TGA) was performed using the 851 Mettler Toledo TGA instrument. The samples were heated from room temperature to 700°C, at a scan rate of 10°C/min, under a nitrogen purge, at a flow rate of 100 mL/min.



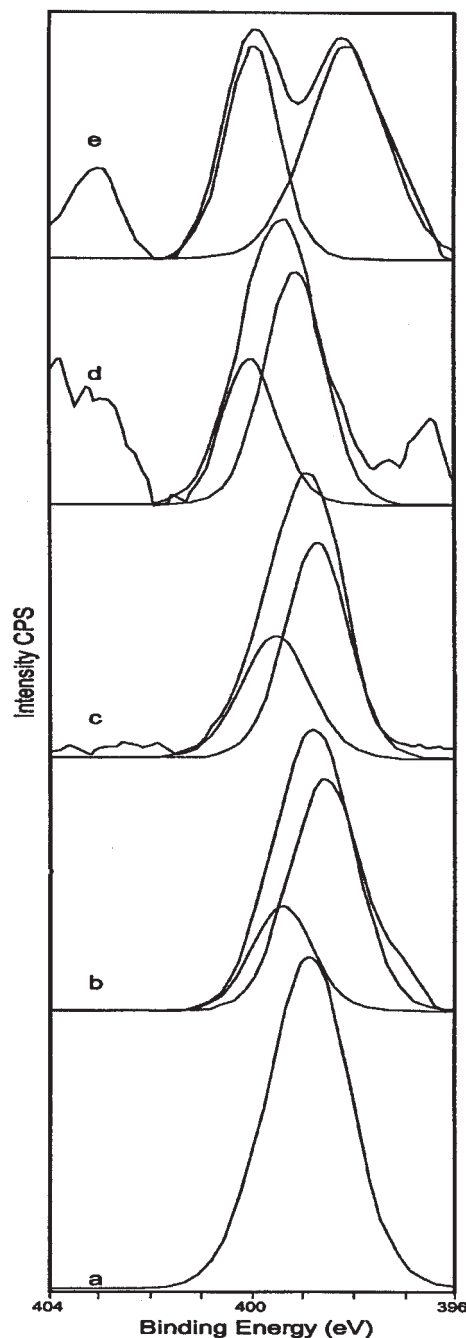
**Figure 1** X-ray diffractograms of copolymer and the composites. (a) Poly(4vp-co-dvb); (b) 2.5 Ce/poly(4vp-co-dvb); (c) 5.0 Ce/poly(4vp-co-dvb); (d) 7.5 Ce/poly(4vp-co-dvb); (e) 10.0 Ce/poly(4vp-co-dvb); and (f) pure CeO<sub>2</sub>.

## RESULTS AND DISCUSSION

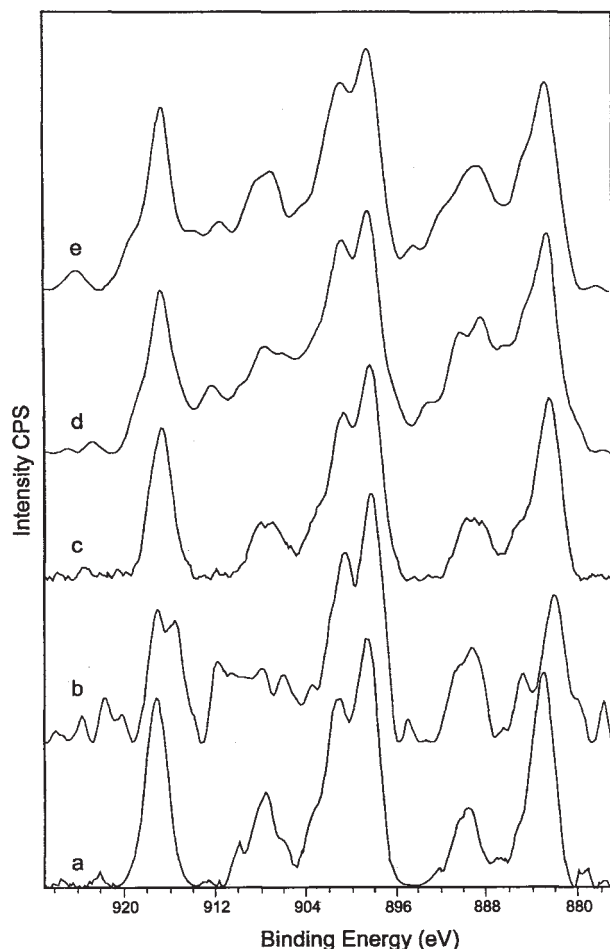
Poly(vinyl pyridine) is an attractive polymer for immobilization of metal nanoparticles, because of the strong affinity of the pyridyl group to metals. In its neutral form, nitrogen atom of pyridine group binds to metals *via* covalent bond by donation of the lone pair of electrons. Lanthanide cations are classified as hard acids and exhibit the capability of complex formation with base nitrogen lone pair of pyridine group, though a weak base with pK<sub>a</sub> value of 5.62.<sup>5,15,16</sup> The reaction of CeCl<sub>3</sub>·7H<sub>2</sub>O and NaOH occurs in the first few hours immediately and is evident with the appearance of reddish orange color, corresponding to the formation of Ce(OH)<sub>4</sub>, which coordinates to the polymer and slowly turns yellow with the formation of CeO<sub>2</sub> over a period of 72 h. It is represented that the thermodynamic driving force for the formation of CeO<sub>2</sub> at room temperature is quite favorable ( $\Delta G = -263$  kJ).<sup>17</sup> However, the kinetics of the reaction was known to be extremely slow because of which a 72-h time period is given for formation of CeO<sub>2</sub> as well as the coordination bond between ceria and nitrogen. The relevant chemical reactions in the formation of ceria on the polymer matrix are expressed as follows. The crystal water molecules are omitted in the equation.



The XRD patterns of the nanocomposites are shown in Figure 1. The pure poly(4vp-co-dvb) has a broad diffraction peak, at  $2\theta = 17^\circ$ , indicating the amorphous nature of the polymer. On composite formation the intensity of the broad peak decreased because of its interaction with cerium. The spectra displayed all the major reflections of CeO<sub>2</sub> with a fluorite (CaF<sub>2</sub>) structure. The diffraction peaks at  $2\theta = 28$  (111),



**Figure 2** XPS of N1s region of copolymer and the composites. (a) Poly(4vp-co-dvb); (b) 2.5 Ce/poly(4vp-co-dvb); (c) 5.0 Ce/poly(4vp-co-dvb); (d) 7.5 Ce/poly(4vp-co-dvb); and (e) 10.0 Ce/poly(4vp-co-dvb).



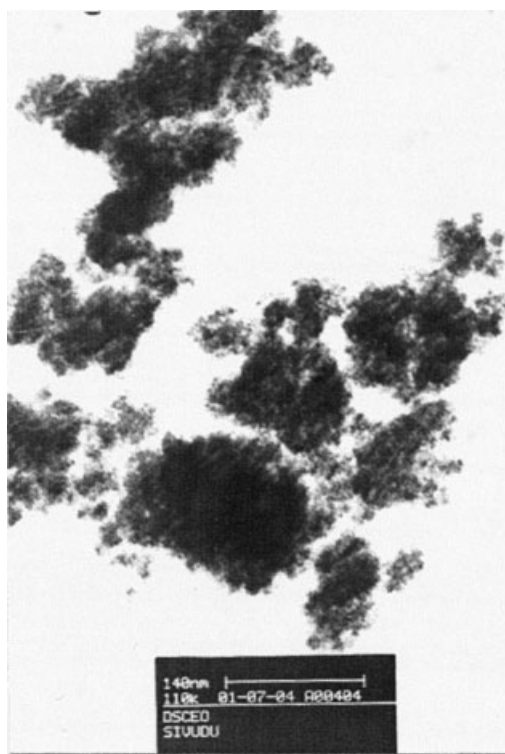
**Figure 3** XPS of Ce 3d-electrons in pure  $\text{CeO}_2$  and  $\text{CeO}_2$  supported on the polymer. (a) Pure  $\text{CeO}_2$ ; (b) 2.5 Ce/poly(4vp-co-dvb); (c) 5.0 Ce/poly(4vp-co-dvb); (d) 7.5 Ce/poly(4vp-co-dvb); and (e) 10.0 Ce/poly(4vp-co-dvb).

31 (200), 48 (220), and 56 (311) of ceria are present in all the composites.<sup>17</sup> However, the weak but distinct reflection peaks indicated that the ceria particles on the polymer were not fully crystalline. On increasing the content of the metal, the intensity of polymer peak at  $2\theta = 17^\circ$  decreases and is almost absent for 10 mol % composite, suggesting a change in the internal packing or folding of the polymer chains in the beads induced by the interaction with the  $\text{CeO}_2$  particles.

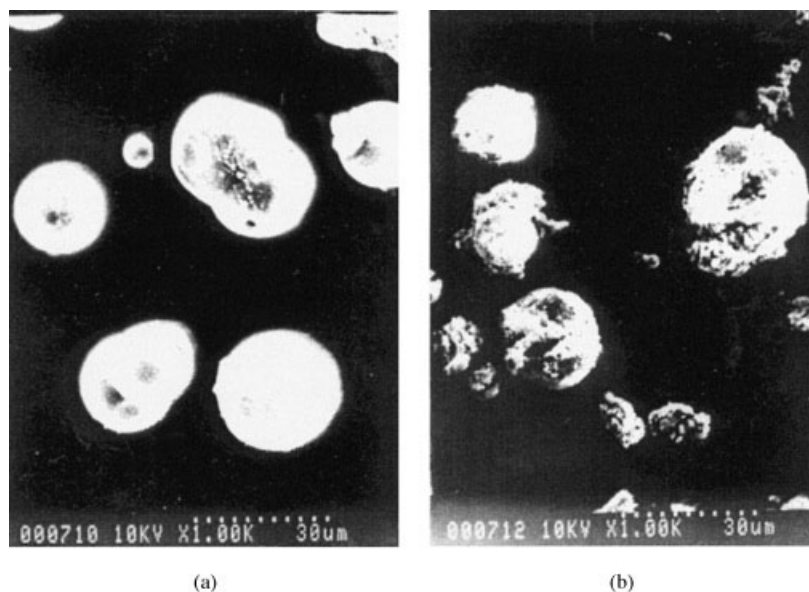
Figure 2 shows the variation in N 1s XPS regions of poly(4vp-co-dvb) and the ceria polymer nanocomposites as a function of increasing metal content. The N 1s peak for the free nitrogen of pyridine group appears at 398 eV.<sup>18</sup> On composite formation, the region exhibited a shift in the spectral envelope toward higher binding energy. The resultant N 1s has shown growth of an additional peak, centered at *ca.* 400 eV, which could be assigned for the metal-coordinated nitrogen. A shift in the peak position to higher binding energies from  $399.4 < 399.6 < 400 < 400.5$  for  $2.5\% < 5\% < 7.5\% < 10\%$ , respectively, was noticed. It is known

from literature that quaternary nitrogen ions are associated with N 1s peak at 401 eV.<sup>19</sup> This new peak at 400 eV, therefore, can be attributed to the quaternary nitrogen on Ce—N bond formation, with the maximum shift and intensity observed for the 10 mol % composite. The ratio of free N to bonded N was found to decrease with increase in the metal content of the composite. Figure 3 shows the region of Ce 3d-electrons of ceria in the composites as a function of the content of cerium. The state of cerium ion having the basic lines with low energy satellites along with the high energy structure reveals the oxidation state of cerium as  $\text{Ce}^{4+}$  in the composites with a strong peak near 916 eV, corresponding to ceria.<sup>20</sup> The spectra rule out the presence of  $\text{Ce}^{3+}$  state because of  $\text{Ce}(\text{OH})_3$  or  $\text{CeCl}_3$  and shows a peak originating from O 1s of ceria nanoparticles at 530.0 and 532.0 eV. For all the nanocomposites examined, the XPS surface compositions of cerium were not found to be same as in the bulk compositions determined by TGA.

The size of the ceria nanoparticles was determined by TEM and is shown in Figure 4. It is seen that the size of the particles was on an average 10–15 nm. SEM is widely used to study the shape, size, and morphology of a polymer surface. The change in the surface morphology of poly(4vp-co-dvb) on complexation with the metal particles was investigated by this technique. Figure 5(a,b) shows the SEM pictures of the polymer microspheres and ceria/polymer composite microspheres, respectively. The pure copolymer mi-



**Figure 4** TEM image of ceria nanoparticles.

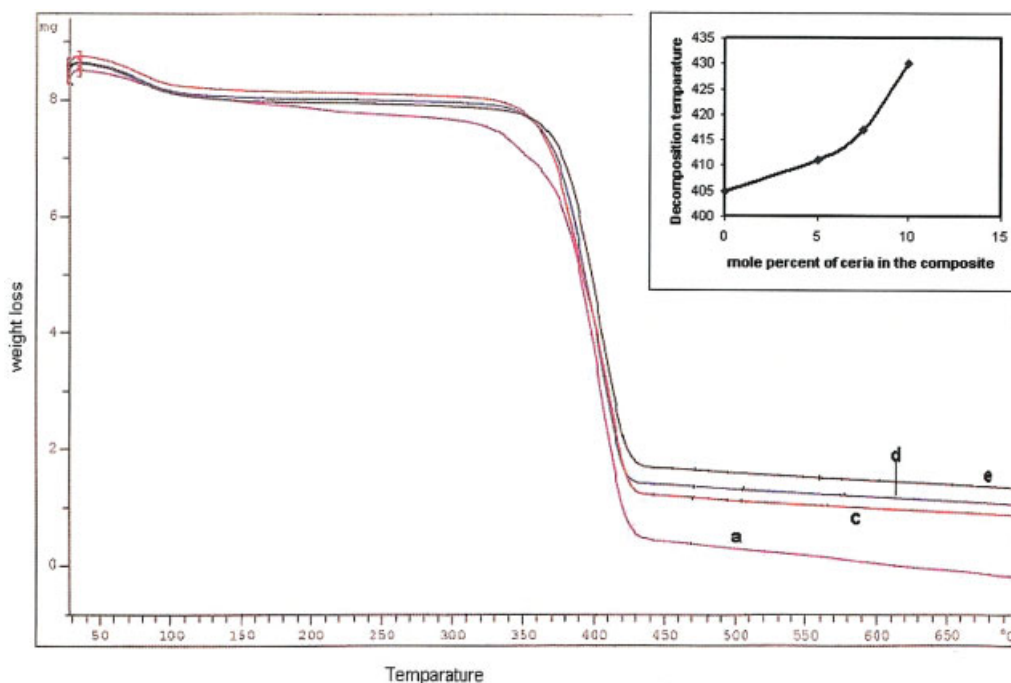


**Figure 5** SEM pictures of (a) poly(4vp-co-dvb) and (b) 10.0 Ce/poly(4vp-co-dvb).

crosspheres were smooth surfaced with a size of *ca.* 50–70  $\mu\text{m}$ . The coordinated ceria particles on the surface are evident from the rough surface, showing a raspberry type of morphology, with large number of ceria particles coordinated on the surface of the polymer microspheres. However, from the higher mass percentage of cerium-coordinated nitrogen peaks in XPS and the estimation of ceria particles from the bulk

compositions, using TGA, the presence of ceria particles inside the polymer microspheres cannot be ruled out.

Thermogravimetry was used to determine the corresponding bulk weight percent of ceria in the nanocomposites (Fig. 6). The copolymer is found to decompose completely at 405°C, while the composites displayed improved thermal stabilities with higher

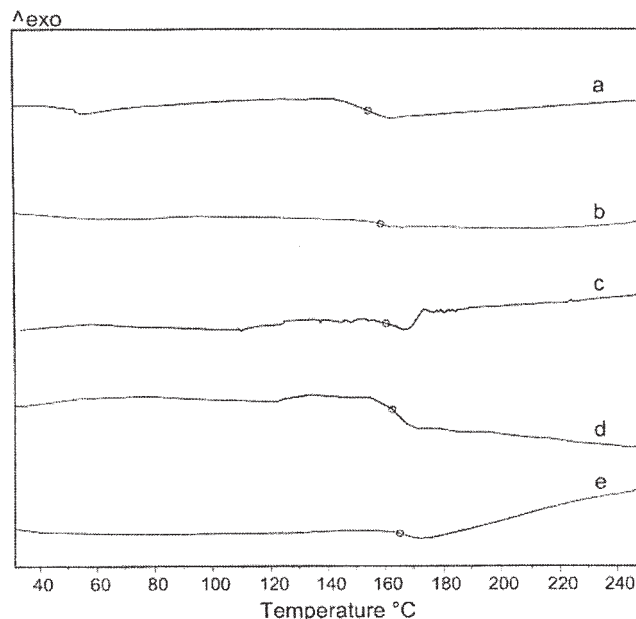


**Figure 6** TGA profiles of the copolymer and composites. (a) Poly(4vp-co-dvb); (c) 5.0 Ce/poly(4vp-co-dvb); (d) 7.5 Ce/poly(4vp-co-dvb); and (e) 10.0 Ce/poly(4vp-co-dvb). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

decomposition temperatures. A maximum of 430°C for the 10 mol % [Fig. 6(e)] was noticed in the differential thermograms of TGA. Such an increase in the decomposition temperature of the composite with increase in the mole percent of ceria from 5.0 < 7.5 < 10.0 indicates that the thermal stability of the composite is directly proportional to the metal content in it. A graph showing the decomposition temperatures versus mole percent of ceria in the composite is shown as a window inside Figure 6. The char yields after decomposition of the polymer component were found to correspond well with the inorganic contents and are listed in Table I. DSC scans of the composites and the copolymer are shown in Figure 7, and the corresponding glass transition temperatures ( $T_g$ ) are listed in Table I. Poly(4vp-co-dvb) exhibits a  $T_g$  at 155°C, and the typical calorimetric (second heating) traces of the composites have shown higher  $T_g$  from that of the pure polymer. A constant increase in the  $T_g$  of the composite, proportional to the metal content, was noticed with a maximum of 166°C for the 10 mol % one. Such enhancement in the  $T_g$  values was earlier reported by Belfiore and coworkers for the poly(vinyl amine)/Eu(III) complexes.<sup>16</sup> However, the increase in the  $T_g$  values in the present work is not similar to those reported by them, which may be due to the rigid structure of the crosslinked polymer in the present work, where the possibility for the microclustering of the polymeric ligands is absent unlike in linear polymers.

## CONCLUSIONS

Incorporation of ceria nanoparticles into poly(4vp-co-dvb) microspheres via in situ reaction of  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  and NaOH at room temperature was performed in one step. Poly(4vp-dvb) microspheres were prepared by free radical suspension polymerization method. On increasing the mole ratio of metal to polymer, crystallite size of the ceria particles has increased, with an average particle size of 7.5–16 nm. The formation of



**Figure 7** DSC scans of the copolymer and composites. (a) Poly(4vp-co-dvb); (b) 2.5 Ce/poly(4vp-co-dvb); (c) 5.0 Ce/poly(4vp-co-dvb); (d) 7.5 Ce/poly(4vp-co-dvb); and (e) 10.0 Ce/poly(4vp-co-dvb).

covalent linkage with the nitrogen atom of the 4vp was confirmed from the binding energies at 400 eV for the quaternary nitrogen. The reaction between the ceria and the polymer was deduced to be mainly through surface reaction mechanism, based on the raspberry morphology, TGA, and XPS data. The thermal stabilities and the glass transition temperatures of the composites increased with increase in the concentration of the metal. Such polymer supported ceria nanoparticles find application as heterogeneous catalysts in organic conversion reactions.

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**TABLE I**  
Cerium Mass Percentages, Glass Transition Temperatures, and Char Yields of the Composites

Sample	Cerium mass <sup>a</sup> (%)	Char yield <sup>b</sup> ( $Y_c$ ) at 700°C (%)	$T_g^c$ (°C)
Poly(4vp-dvb)	—	—	155
2.5 Ce/poly(4vp-dvb)	—	4.50	159
5.0 Ce/poly(4vp-dvb)	13.63	10.06	160
7.5 Ce/poly(4vp-dvb)	28.89	12.31	162
10.0 Ce/Poly(4vp-dvb)	33.62	15.55	166

<sup>a</sup> By XPS.

<sup>b</sup> By TGA.

<sup>c</sup> By DSC.

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