Emulsion Polymerization of Ethylene from Mesoporous Silica Nanoparticles with Vinyl Functionalized Monolayers

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ABSTRACT: Emulsion polymerization of ethylene from vinyl functionalized mesoporous silica nanoparticles (V-MSNs) was reported. V-MSNs were synthesized via deposition of vinyl monolayers on the pore walls, and the relative surface coverage of the vinyl monolayers was 74%. A fluorinated P-O-chelated nickel catalyst coordinated to the vinyl groups. These V-MSNs hosting catalysts were full dispersed in water assisted by ultrasonic processor in the presence of surfactants. After addition of ethylene, polyethylene (PE) chains grew from the pores of V-MSNs, formation of stable nanocomposite latices with solid content up to 17.3%. Our method made V-MSNs well-dispersed in the PE matrix. Especially, because of a strong interaction between PE and nanoparticles, a stable V-MSNs core/PE shell structure was formed upon thermal treatment above melting temperature of the PE. Samples were analyzed by a number of techniques including TEM, N2 adsorption-desorption, FTIR, and solid state 29Si NMR, DLS, 1H NMR, GPC, and DSC. © 2009 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 47: 1393–1402, 2009
Keywords: emulsion polymerization; mesoporous silica nanoparticles; nanocomposite; polyethylene

INTRODUCTION

Extensive research has focused on mixture of polymer and inorganic nanofillers to enhance properties of polymer and introduce novel properties.1,2 However, to full disperse nanoparticles in the polymer matrix is a big challenge.2 Among a great variety of methods for preparation of nanocomposites, miniemulsion polymerization in the presence of inorganic nanoparticles was found to be a suitable route for the preparation of well-dispersed nanocomposites with various morphologies.2,3 In this system, inorganic nanoparticles were dispersed in the miniemulsion monomer droplets. After polymerization, these nanoparticles are embedded in the polymer matrix. At first, the miniemulsion technology was restricted to free radical polymerization because of the poisoning effect of water on most nonradical active species (anionic, cationic organometallic ones).3,4 Recently, this technology was successfully applied for preparation of polyethylene (PE)/silica nanocomposites using water tolerant nickel catalysts.2

A key aspect in preparation of polymer/filler composites is to enhance the bonding between polymer and fillers.2,5 Both theory and experimental results have confirmed that a good interaction between polymer matrix and fillers leads to improved mechanical properties.6–9 When polymers are strongly absorbed on the surface of inorganic nanoparticles, a nanoparticles core/polymer shell structure could be obtained.1,10 PE and silica
are perhaps the simplest and most common organic and inorganic polymer, respectively, but the synthesis of well-dispersed PE/silica nanocomposites with good interaction between PE and fillers is a challenge because of the general difficulty in handling PE, which is devoid of any functional group.11 Anchoring a catalyst onto the filler surface, and then PE chains grow directly from the surface of fillers has proven to be a suitable route for preparation of nanocomposites with enhanced interfacial adhesion.12 This method has been applied for a board range of nanofillers, such as clay,13 silica,14 and carbon nanotubes.15

In this paper, we report on the synthesis of mesoporous silica nanoparticles (MSNs)/PE nanocomposites via polymerization of ethylene from MSNs using miniemulsion technology. When compared with silica nanoparticles, MSNs (typical particle sizes are 50–300 nm) possess high surface area (may larger than 1000 m²/g) and the easily accessible, uniformly sized pores (pore sizes vary from 2 nm to 10 nm).16–18 These features make MSNs excellent candidates for hosting molecules of various sizes, shapes, and functionalization.16–19 Furthermore, the utilization of very small particles improves the mass transfer into or out of the pore system.20 Herein, we functionalized the internal surface of MSNs with vinyl monolayers (samples denoted as V-MSNs). Then a fluorinated P-O-chelated nickel catalyst coordinated to the vinyl groups. These MSNs hosting catalysts (V-MSN-cats) were dispersed in water assisted by ultrasonic processor in the presence of surfactants. After the addition of ethylene, polyethylene chains grew from the pores of V-MSNs, formation of stable nanocomposite latices. Our method made the nanoparticles well-dispersed in the PE matrix and a stable latex with high solid content was obtained. Especially, because of the strong interaction between PE and V-MSNs, a stable V-MSNs core/PE shell structure was formed upon thermal treatment above melting temperature of the PE. For comparative purposes, the ethyl groups without the possibility of coordinating to the catalysts were also grafted onto the pore walls of MSNs (samples denoted as E-MSNs) in this study.

EXPERIMENTAL

Materials

Bis(1,5-cyclooctadiene)nickel [Ni(COD)₂] and Ethyl 4,4,4-trifluoro-2-(triphenylphosphoranylidene)-acetoacetate (ETPA) were purchased from Aldrich. Other reagents were purchased from Shanghai Reagents. Toluene was dried over 10 Å molecular sieves for 10 days and then refluxed over Na for 10 h. Ultrapure water (σ = 18.2 MΩ cm) was degassed and decarbonated with argon.

Characterization

Surface analysis of samples was performed on a Micromeritics ASAP 2010 analyzer at the temperature of liquid nitrogen. The surface areas were calculated by the Brunauer-Emmett-Teller (BET) and pore size distribution was measured by Barrett-Joyner-Halenda (BJH) methods. Samples were outgassed at 100 °C for 12 h before analysis. The pore volume was taken at a relative pressure of 0.99.

Solid state ²⁹Si NMR experiments were recorded on Bruker DSX 300 NMR. The following experimental parameters were used: 4.0 KHz spinning frequency, 45° pulse width of 2.4 μs, 30 s recycle delay, 360 scans. FTIR spectra were obtained using a Bruker Vertex 70 spectrophotometer using KBr pellets. Molecular weights and molecular weight distribution (MWD) of the polyethylene were measured in 1,3,4-trichlorobenzene at 150 °C using PL 220 GPC instrument (Polymer Laboratories). Three PL mixed-B columns (500–10⁷) were used. Universal calibration against narrow polystyrene standards was adopted (Universal calibration: K (PS) 12.1, α(PS) 0.707, K(sample) 59.1, α(sample) 0.69. Before analysis of the samples using GPC, the inorganic nanoparticles were removed from the PE matrix with chemical etching procedure in a solution of hydrofluoric in 2-propanol (HF/C₃H₇OH in 4:1 volumetric ratio). Differential scanning calorimetry (DSC) was carried out with a PERKIN-ELMER at a heating rate of 10 °C/min from 0 °C to 200 °C. Dynamic light scattering (DLS) on latex samples was performed on a HPPS Malven particle sizer. Hydrogen nuclear magnetic resonance (¹H NMR) spectra were measured with Bruker AVANCE III 400 MHz spectrometer using deuterated benzene as solvent. ¹H NMR chemical shifts were referred to TMS as an internal standard. High-temperature NMR measurements were performed in 1,1,2,2-tetrachloroethane-d₂ at 120 °C. The TEM images were obtained from JEOL 2100 operating at 200 kV. The samples were prepared by evaporation of a drop of latex on a grid at room temperature. These samples were also annealed at 130 °C for 1 h for further characterization by TEM.
Preparation and Functionalization of MSNs

MSNs were synthesized according to a reported method. Typically, 1 g of cetyltrimethylammonium bromide (CTAB) was dissolved in a solution of 480 mL water and 3.5 mL of 2 M NaOH. Mesitylene (7.0 mL) was then added to the solution. The mixture was stirred vigorously at 80 °C for 2 h, following which tetraethyl orthosilicate (5.0 mL) was added dropwise. The reaction mixture was stirred for further 2 h at 80 °C. The resulting precipitate was collected by filtration, washed with methanol, and dried under vacuum at 100 °C for 24 h. The surfactant templates and mesitylene were extracted from the samples using HCl/methanol solution. A suspension of 1.0 g of the as-synthesized MSNs were stirred for 6 h at 50 °C in 100 mL methanol with 0.75 mL concentrated hydrochloric acid. The template-removed product was then collected via filtration and dried under vacuum at room temperature for 12 h.

The procedure for functionalization of MSNs with vinyl monolayers was described as follows: 1 g of MSNs (1095 m² of surface area) was suspended in 50 mL of dried toluene. To this mixture was added 0.2 mL of water (6.1 × 10¹⁸ water molecules/m², slightly more than the number of silanols present on a fully hydroxylated silica surface). The suspension was stirred vigorously for 3 h at room temperature to allow the water to disperse through the mesoporous matrix. Then 1.75 mL of vinyl-trichlorosilane was added via syringes and the mixture was stirred for 12 h at room temperature. The product (V-MSNs) was collected by filtration, washed with plenty of 2-propanol, and dried under vacuum. Same procedure was used to functionalization of MSNs with ethyl groups (E-MSNs), except that 1.81 mL of ethyl-trichlorosilane was added.

Aqueous Catalytic Polyemrization of Ethylene

In a Schlenk bottle, 0.1 g of Ni(COD)₂, 0.1 g of ETPA, and 0.2 g of V-MSNs were added into 2 mL of toluene. This thick slurry was stirred for 40 min and a black brown supported catalysts were obtained. These supported catalysts were added into 100 mL of water containing 1 g of sodium dodecyl sulfate (SDS) and 0.3 mL of hexadecane in a flask. The mixture was then emulsified with a 600 W ultrasonic sonifier for 3 min. The dispersed mixture was transferred into a 400 mL stainless steel reactor. After the temperature reached 60 °C, the reactor was flushed, and pressured with ethylene under mild stirring (360 rpm). After the required reaction time (4 h), ethylene was vented slowly enough to avoid latex flocculation after polymerization. The latex was taken for analysis by TEM and DLS. For determination of the solid content, methanol was added into the latices. The precipitated PE was washed with methanol and dried under vacuum. Same procedure setup was adopted when E-MSNs was used (entry 5, Table 2). For comparative purposes, the catalysts dissolved in toluene without nanoparticles were used for emulsion polymerization of ethylene under same condition (entry 1, Table 2).

RESULTS AND DISCUSSION

Synthesis and Functionalization of MSNs

We synthesized MSNs with large pores by adding a pore-expanding agent (mesitylene) to a CTAB-templated, base-catalyzed condensation reaction of silicate that have been reported. As shown in the TEM, MSNs have a particle diameter of 100–200 nm and composed of order hexagonal array of mesoporous channels [Fig. 1(a)]. The nitrogen surface sorption analysis of MSNs gave the BET surface area of 1095 m²/g⁻¹ and the pore size of 6.5 nm.

The V-MSNs were synthesized via deposition of organosilanes on the pore walls. In this process, the surface of MSNs was prehydrated with 1.2 monolayers worth of water, followed by treatment with slight (ca.20%) excess of organosilanes (based on the available surface area). The organosilanes (vinyl-trichlorosilane or ethyl-trichlorosilane in our case) then underwent hydrolysis and became covalently attached to the substrate and crosslinked to one another. This method is very efficient in deposition of high-quality organic monolayers on the pore walls up to 100% surface coverage. Figure 1 shows the structure of V-MSNs. The functionalization of MSN with vinyl monolayer did not destruction the ordered structure.

To confirm the grafting of the organosiloxanes onto the pore walls of MSNs, the samples were analyzed by solid state ²⁹Si NMR, FTIR, and N₂ adsorption. The ²⁹Si NMR spectra (Fig. 2) show the peaks at −110 ppm (Q⁴) and −101 ppm (Q³), [Qⁿ = Si(OSi)ₙ(OH)₄₋ₙ, n = 2–4], which are assigned to fully crosslinked silica and silica with one terminal hydroxyl group, respectively. Integration of the Q³ and Q⁴ peaks shows that the Q³ peak areas decreased significantly after
functionalization of MSNs with organosiloxanes, suggesting the covalent bonding of the organosiloxanes to the \(-\text{Si}--\text{OH}\) groups of MSNs (Q$^3$) to form full crosslinked Si--O--Si bonds (Q$^4$). The covalent bonding of functional groups to MSNs is also evidenced by the presence of two additional peaks, T$^2$ and T$^3$ [$T^2 = \text{R-Si-(OSi)}_2(\text{OH})$, $T^3 = \text{R-Si-(OSi)}_3$, $\text{R} = -\text{CH=CH}_2$ or $-\text{CH}_2\text{CH}_2$] in the functionalized MSNs. These peaks are ascribed to the resonances of the incorporated organosiloxanes in the functionalized MSNs.

FITR spectra further confirmed the functional groups grafted onto MSNs (Fig. 3). The peaks around 2967–2855 cm$^{-1}$, which were assigned to the aliphatic C--H vibrations, were observed in the ethyl-functionalized samples. The alkene...
C–H vibration (3067 cm\(^{-1}\)) and C–C stretching vibration (1604 cm\(^{-1}\)) were observed in the vinyl-functionalized samples.

Table 1 lists the BET surface areas, BJH pore sizes, and pore volumes of the different materials. As seen from Table 1, functionalization of MSNs with vinyl or ethyl groups results in a marked decrease in BET surface area, a reduction of the pore volume and shrinkage of the BJH pore diameter. These results are consistent with the presence of a significant amount of grafted species attached to the pore walls.\(^{20,25}\) The surface coverage of the functional groups was estimated by gravimetric method.\(^{23}\) After functionalization, the mass of MSNs increased by 60%, and 58% for V-MSNs and E-MSNs, respectively. Based on the weight obtained (W%), the surface area (SA) the molecular weight (\(M_n\)) of the functional groups [OH–Si–(O)–R],\(^{25}\) and assumption of \(5 \times 10^{18}\) molecules per square meter in a full dense monolayer coverage,\(^{21}\) surface coverage (\(X\)) can be calculated from

\[
X = \frac{[W\%/M_n]}{6.02 \times 10^{23} / (SA \times 5 \times 10^{18})}
\]

Here, 74% and 72% surface coverage was obtained for V-MSNs and E-MSNs, respectively. These V-MSNs with high surface coverage are desirable for anchoring metal catalysts onto the nanopores for ethylene polymerization due to their advantages: high surface coverage with organic groups obviating the destructive interaction of reactive catalysts with silanol groups (Si–OH) lining the framework pore walls; high density of vinyl groups making catalysts easy coordinate to the vinyl groups; hydrophobic surface contributed by vinyl groups preventing catalysts from poison by water, which is particularly beneficial to ethylene polymerization in aqueous phase.

**Attachment of Catalysts onto the Nanopores**

A fluorinated P-O-chelated nickel complex, which is high activity and water-tolerant,\(^{4,26,27}\) was chosen for catalytic ethylene polymerization. These catalysts are obtained by complexation of a fluorinated ylide onto Ni(COD)\(_2\).\(^{26,27}\) Upon addition of olefins, the ligated COD is displaced by ylides and formation of active complexes via coordinating to the olefins (Scheme 1).\(^{26,27}\) V-MSNs possess high surface area and high density of vinyl groups in the nanopores. This feature made it easy to attach the catalysts onto V-MSNs via coordinating to the vinyl groups (the resulting samples denoted as V-MSN-cats). Indeed, when the solution of Ni(COD)\(_2\) and ylides was mixed with V-MSNs, the solution turned immediately from light yellow to black brown. No change in the color was observed when E-MSNs were used. The formation of active

![Figure 2. Solid state \(^{29}\)Si NMR spectra: (a) MSNs; (b) V-MSNs; (c) E-MSNs. \(^{Q}\) \(^{3}/Q^{4}\) indicated the ratio of the peak areas.](image)

![Figure 3. FTIR spectra: (a) MSNs; (b) V-MSNs; (c) E-MSNs.](image)

**Table 1. Properties of MSNs and Functionalized MSNs**

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET Surface Area/m(^2)/g(^{-1})</th>
<th>BJH Pore Size/nm</th>
<th>Pore Volume/cm(^3)/g(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSN</td>
<td>1095</td>
<td>6.5</td>
<td>2.0</td>
</tr>
<tr>
<td>V-MSN</td>
<td>512</td>
<td>5.26</td>
<td>0.61</td>
</tr>
<tr>
<td>E-MSN</td>
<td>542</td>
<td>5.15</td>
<td>0.67</td>
</tr>
</tbody>
</table>

V-MSNs and E-MSNs, respectively. Based on the weight obtained (W%), the surface area (SA) the molecular weight (\(M_n\)) of the functional groups [OH–Si–(O)–R],\(^{25}\) and assumption of \(5 \times 10^{18}\) molecules per square meter in a full dense monolayer coverage,\(^{21}\) surface coverage (\(X\)) can be calculated from

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complexes was further confirmed by $^1$H NMR, because the free and the ligated COD protons display notably different resonances. The solution of Ni(COD)$_2$ and ylides was mixed with V-MSNs at room temperature [molar ratio of Ni(COD)$_2$, ylides and vinyl groups was 1:1:2], the resonances of COD protons shifted from 4.29 ppm (ligated form) to 5.64 (free form) for vinylic protons and from 2.02 (ligated form) to 2.30 (free form) for the allylic ones. No changes in the resonances of the COD protons were observed in the absence of V-MSNs. These results confirmed the displacement of COD by the ylides in the presence of V-MSNs, and formation of the active complexes via coordinating to the vinyl groups.

**Emulsion Polymerization of Ethylene**

Before the polymerization, V-MSN-cats or E-MSN-cats, which are dispersed in a small amount of toluene, were full dispersed in the water (containing surfactants and hydrophobe) to form emulsion by a high shear generated by an ultrasonic processor. DLS shows that the particle sizes of V-MSN-cats and the droplet size of toluene emulsion was 149 and 167 nm, respectively. The droplets size of the mixture of V-MSN-cats and toluene emulsion was 206 nm, suggesting the interaction between the V-MSN-cats and the toluene phase. We assume that the V-MSN-cats were dispersed in toluene droplets in the initial state of polymerization mixture. NMR results have confirmed that few free catalysts were dissolve in toluene after the catalysts were coordinated to vinyl groups in the nanopores. The well-dispersed V-MSNs can be viewed as ethylene polymerization nanoreactors, where polyethylene chains grow upon addition of ethylene.

The results of polymerization of ethylene are shown in Table 2. Generally, V-MSN-cats show higher activity than E-MSN-cats or the catalysts without nanoparticles. The attachment of surfactants and hydrophobe to form emulsion by a high shear generated by an ultrasonic processor. DLS shows that the particle sizes of V-MSN-cats and the droplet size of toluene emulsion was 149 and 167 nm, respectively. The droplets size of the mixture of V-MSN-cats and toluene emulsion was 206 nm, suggesting the interaction between the V-MSN-cats and the toluene phase. We assume that the V-MSN-cats were dispersed in toluene droplets in the initial state of polymerization mixture. NMR results have confirmed that few free catalysts were dissolve in toluene after the catalysts were coordinated to vinyl groups in the nanopores. The well-dispersed V-MSNs can be viewed as ethylene polymerization nanoreactors, where polyethylene chains grow upon addition of ethylene.

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catalysts onto the ordered nanopores seems to reduce the possibility of deactivation during polymerization. This behavior was also observed when metallocene catalysts were anchored onto ordered nanopores.28,29 In the case of E-MSN-cats, the catalysts were dissolved in the organic droplets without the possibility of attachment onto the nanopores. The activity of E-MSN-cats is comparable to that of the catalysts without nanoparticles. Increase in the ethylene pressure resulted in a higher activity. This was explained by more ethylene dissolved in water and in the polymer particles at higher pressure.4

A stable latex with up to 17.3% solid content was obtained after polymerization. The surfactant concentration of 1% is high enough to stabilize the latices. Increase in the surfactant concentration did not result in more stable latices. The latex particle sizes measured by DLS were about 570 (entry 2, Table 2) and 200 nm (entry 5, Table 2) for the samples produced by V-MSN-cats and E-MSN-cats, respectively. The difference in the particle sizes might imply a different mechanism for the formation of composite particles when V-MSN-cats and E-MSN-cats were used. In the case of V-MSNs, because the catalysts can be covalently attached onto the pore walls, the PE chains grew from the surfaces of MSNs, resulting in a large particle size. For E-MSN, because the catalysts were dissolved in the organic droplets without the possibility of attachment onto E-MSNs, the composite particles were generated from organic droplets, resulting in relatively smaller composite particles.

### Table 2. The Results of Emulsion Polymerization of Ethylene

<table>
<thead>
<tr>
<th>Entry</th>
<th>MSNs</th>
<th>Ethylene Pressure/atm</th>
<th>c_{sdw} (%)</th>
<th>Solid Contentb (%)</th>
<th>Activity/×g (PE) mol (cat⁻¹) h⁻¹</th>
<th>Crystallinityc (%)</th>
<th>Mₙd (NMR)</th>
<th>Mₙe (GPC)</th>
<th>MWD (GPC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nof</td>
<td>40</td>
<td>1</td>
<td>10.0</td>
<td>6.87 × 10³</td>
<td>48</td>
<td>882</td>
<td>3447</td>
<td>4.4</td>
</tr>
<tr>
<td>2</td>
<td>V-MSN⁵</td>
<td>40</td>
<td>1</td>
<td>17.3</td>
<td>1.19 × 10⁴</td>
<td>24</td>
<td>707</td>
<td>1247</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>V-MSN</td>
<td>40</td>
<td>2</td>
<td>15.0</td>
<td>1.03 × 10⁴</td>
<td>37</td>
<td>763</td>
<td>1083</td>
<td>2.2</td>
</tr>
<tr>
<td>4</td>
<td>V-MSN</td>
<td>20</td>
<td>1</td>
<td>4.8</td>
<td>3.30 × 10³</td>
<td>35</td>
<td>826</td>
<td>1306</td>
<td>2.1</td>
</tr>
<tr>
<td>5</td>
<td>E-MSN</td>
<td>40</td>
<td>1</td>
<td>9.6</td>
<td>6.50 × 10³</td>
<td>55</td>
<td>1029</td>
<td>5011</td>
<td>4.1</td>
</tr>
</tbody>
</table>

* Concentration in the volume of water.
* Solid content determined by gravimetry of the filtered latex.
* This was measured based on a melting enthalpy of 293 J/g for 100% crystalline PE.13
* These data were measured by ¹H NMR.
* These data were measured by GPC.
* No MSNs in this system.
* The density of V-MSN was 0.13 g/cm³.

![Figure 4. TEM micrographs of nanocomposite dispersions: (a) PE/V-MSNs (The arrows indicated the PE films); (b) PE/E-MSNs.](image-url)
The $^1$H NMR analysis of the PE end groups (total double bond content by $^1$H)$^{27}$ shows that each polymer is a low molecular weight material, which is in agreement with the GPC results (Table 2). Both GPC and NMR results also indicated that the molecular weights of PE produced from V-MSN are lower than that of pure PE (entry 1, Table 2) and of the PE produced from E-MSN (entry 5, Table 2). Because the catalysts were coordinated to the vinyl groups in the nanopores and few catalysts were dissolved in toluene drops, upon addition of ethylene, the copolymerization of PE with the vinyl groups and growth of the PE chains from the nanopores could be expected. The

Figure 5. TEM micrographs of nanocomposite dispersions after annealing for 1 h at 130 °C: (a) PE/V-MSNs; (b,c) PE/E-MSNs.
lower molecular weight of polymer observed with V-MSN could be due to the copolymerization of PE with the vinyl groups.\textsuperscript{27}

When compared with PE/E-MSNs, a lower crystallinity of PE was observed for PE/V-MSNs (Table 2). This behavior was explained by the lower molecular weight of PE in PE/V-MSNs and the restriction to crystallinity imposed by the constrained pore walls from which the PE chains grew.\textsuperscript{30,31}

**Morphology of PE Composites**

Microscopic imaging analyses by TEM are depicted in Figure 4. A homogeneous dispersion of functionalized MSNs in the PE matrix was observed when V-MSNs or E-MSNs was used, confirming that the miniemulsion method produced good nanoparticle dispersion. We failed to observe the individual composite particles (one nanoparticle core/PE shell) due to the easy coalescence of composite particles during the evaporation of water for the preparation of TEM samples.

After the composite samples obtained with E-MSNs and V-MSNs were annealed above the melting point of PE, a significant difference in the microstructure was observed (Fig. 5). In the case of PE/V-MSNs, a clear nanoparticle core/PE shell structure was observed after annealing [Fig. 5(a)]. As for PE/E-MSNs, the nanoparticles were aggregated together [Fig. 5(b)] or fully separated from the PE matrix and deposited on the substrate [Fig. 5(c)]. It is known that the mobility of nanoparticles in the polymer becomes much higher during annealing. Only a physical interaction existed between PE and E-MSNs. During annealing, both coalescence of E-MSNs and full separation of E-MSNs from the PE matrix occurred. In the PE/V-MSNs system, the increase in the size of nanoparticles due to the neighboring particles approach was also observed upon annealing, but further aggregating of these particles to generate larger ones can be spatially hampered by the grafted PE chains, leading to a core/shell structure. This core/shell structure can be retained even after a longer time annealing (such as 2 h), suggesting an intimate interaction between PE and V-MSNs.

**CONCLUSIONS**

MSNs with vinyl functionalized monolayers were prepared and used for hosting nickel complexes for catalytic polymerization of ethylene in emulsion. Our method can produce stable PE/MSNs nanocomposite latices. Additionally, because of a strong interaction between PE and nanoparticles, a stable nanoparticles core/PE shell structure was observed upon annealing these samples. In principle, other catalysts or initiators are also feasible to be attached onto the pore walls of MSNs via rational design of the surface of nanopores, which would lead to a variety of MSNs-based nanocomposites with good interaction between polymer and fillers.

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**REFERENCES AND NOTES**