Direct Grafting of ε-Caprolactone on Solid Core/Mesoporous Shell Silica Spheres by Surface-Initiated Ring-Opening Polymerization

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ABSTRACT: Poly(ε-caprolactone) (PCL) was formed on Solid core/mesoporous shell (SCMS) silica surface by surface-initiated ring-opening polymerization (SI-ROP). The SI-ROP of ε-caprolactone was achieved by heating a mixture of SCMS silica, ε-caprolactone and the tin(II) 2-ethylhexanoate [$Sn(Oct)_2$] in a anhydrous toluene for 20 h at different temperatures viz. 40, 60, and 80°C. The PCL grafted SCMS silica was characterized by fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), X-ray, differential scanning calorimetry and scanning electron microscopy (SEM). The FTIR spectroscopic analysis reveals the formation of ester linkage between PCL and hydroxyl terminated SCMS silica. TGA investigation shows increase in PCL content on SCMS silica surface with increase in reaction temperature. The SEM photographs clearly show the formation of PCL polymer on the SCMS silica surface without altering the spherical nature of SCMS silica. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2689–2694, 2008

Key words: poly(ε-caprolactone); ring-opening polymerization; solid core/mesoporous shell silica; infrared spectroscopy; thermogravimetric analysis

INTRODUCTION

The coating of solid substrates with biocompatible and/or biodegradable polymers has drawn a great deal of attention because of its potential applicability to biomedical areas such as passivation of prosthetic devices and implants, coating for drug-delivery devices, and scaffolds for tissue engineering.[1–4] For polymeric coating of substrates, the ''grafting-from'' approach, based on surface-initiated polymerization (SIP), has intensively been studied because of its inherent superiority over the other conventional techniques such as spin-casting and ''grafting-onto'' approach, in the aspects of robustness and controllability of density and thickness.[5–7] In the process of SIP, polymer brushes are grown from initiators bound to surfaces by reacting with monomers in solution. Among various types of polymers, polymeric films of biocompatible and biodegradable aliphatic polyesters, such as poly(lactic acid) (PLA), poly(ε-caprolactone)(PCL), and poly(*p*-dioxanone) (PPDO), were prepared by surface-initiated ring-opening polymerization (SI-ROP).[8–14]

There have been many efforts for polymeric coating of aliphatic polyesters on a variety of solid substrates via SI-ROP.[8–14] Similar to synthesis in solution or bulk, organometallic catalysts, such as $Sn(Oct)_2$ and $AlEt_3$, have generally been employed for SI-ROP of biodegradable aliphatic polyesters from surfaces presenting hydroxyl or amino groups. For example, Yoon and Choi reported the use of $Sn(Oct)_2$ to produce PPDO brushes on gold and silicon oxide surfaces by ROP of *p*-dioxanone[8] and Husemann et al. used diethylaluminium alkoxides prepared from $AlEt_3$ as a catalyst to grow PCL brushes from gold surfaces presenting hydroxyl groups[9]. Similar reaction conditions have widely been applied to SI-ROP for coating of various aliphatic polyesters, such as PLA,[8,10] PCL,[10,11] and PPDX[11–13] on various types of substrates, such as gold,[8–11] silicon oxide[8,11,12] and nanotubes.[13] In addition to the flat solid substrates, micro- and nanoparticles have also been used for surface initiated polymerization.[15,16] Polymer-grafted micro- and nanoparticles, and hollow micro- and nanoparticles could find their applications in biomedical sciences particularly as drug delivery systems and cell cultures.

In this study, we prepared a polymeric sphere of PCL on solid core/mesoporous shell (SCMS) silica surface by SI-ROP of ε-caprolactone with $Sn(Oct)_2$ as a catalyst. $Sn(Oct)_2$ is the one of the most widely used compounds for initiating the ring opening polymerization of various lactones and lactides. $Sn(Oct)_2$ has been approved for surgical and

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pharmacological applications by the US Food and Drug Administration. The use of insoluble supports to mediate organic transformations has been developed extensively over the years. One of the common transformations in solid-phase organic synthesis involves the construction of an ester linkage between a solid support and the other monomer. The ester linkage has good stability to a variety of reaction conditions, while different strategies generate such an ester linkage on solid support is available. In this research, authors studied one of the convenient and straightforward method involving ring opening polymerization of ε-caprolactone on hydroxyl bound SCMS silica. Kolbe[17] reported the synthesis of nonporous monodisperse silica particles based on the hydrolysis and subsequent condensation of silicon alkoxides in a short-chain alcohol as solvent. Later Stober et al.[18] were able to synthesis nonporous spherical silica particles. Further studies have shown that in the initial phase of the reaction the silicon alkoxide hydrolyzes and oligomers are formed as seeds. Subsequently, monomers and smaller oligomers aggregate on these seeds and form the resulting silica particles. On the basis of Stober reaction, Kaiser[19] prepared porous silica beads by cohydrolysis and subsequent condensation of tetraethoxysilane and an *n*-alkyltrialkoxysilane in a mixture of ethanol, water, and aqueous ammonia. Ethanol act as a cosolvent to form a homogeneous solution, ammonia serves as a morphological catalyst, and *n*-alkyltrialkoxysilane has the function of a porogen to generate the porosity. After the bead formation and drying, the porogen is removed by calcinations leading to porous particles. Thus, nanocomposite materials, in which the organic phase consists of biopolymers, are of special interest. Poly(ε-caprolactone) (PCL) is one such perspective polymers, possessing the linear chain structure. It is also worth to point out PCL is a biocompatible and biodegradable aliphatic polyester, well known for a valuable set of properties such as nontoxicity for living organisms, resorption after an appropriate period of implantation and good ultimate mechanical properties.[20] These surface grafted (SCMS silica-*g*-PCL) particles can be employed as catalytic supports or as highly efficient packing in high-resolution separations such as high-performance liquid chromatography and electro-chromatography.[21]

EXPERIMENTAL

Materials and methods

Tetraethoxysilane, absolute ethanol and aqueous ammonia were obtained from Merck, Germany. $Sn(Oct)_2$ was purchased from Sigma, USA. ε-caprolactone was kindly provided by Samyang company, Korea. Tetraethoxysilane was distilled in vacuum immediately before use. Toluene (from Aldrich) was purified by distillation over sodium. All other solvents and reagents were analytical-grade and used as received.

Synthesis of solid core/mesoporous shell silica spheres

Absolute ethanol (1.27 mol) and aqueous ammonia (32 wt %, 0.17 mol) were mixed in a flask. After the mixture had been heated to 30°C, tetraethoxysilane (0.026 mol) was added rapidly. The solution was mixed for 5 min by shaking to ensure homogeneity. After 1h, a mixture of tetraethoxysilane (0.022 mol) and *n*-octadecyltrimethoxysilane (2.36 mmol) was added drop by drop over a period of 20 min, while stirring with a magnetic stirrer. After the mixture was added, the stirring was stopped and the solution was kept at ambient temperature for 1 h. The solvent was removed in vacuum at 60°C using a rotary evaporator and the resulting white powder was dried overnight at 100°C. To remove the porogen, the powder was subjected to calcinations in air for a period of 6 h at 550°C at a heating rate of 1°C/min.

Surface-initiated ring-opening polymerization of ε-caprolactone

The SCMS silica ball was vacuum dried at 80°C immediately before the use. The vacuum dried SCMS silica ball (2.1 g) along with dehydrated toluene (20 mL) was taken in clean round bottom flask fitted with mechanical stirrer. The catalyst $Sn(Oct)_2$ (0.5 mmol) was added dropwise through dropping funnel slowly. The monomer, ε-caprolactone (5 mL), was then added by syringe to the mixture maintained at different temperatures viz. 40, 60, and 80°C and stirred for 20 h. The resulting mixture containing SCMS silica-*g*-PCL was centrifuged at 1200 rpm for 30 min to remove the solvent. The SCMS silica-*g*-PCL was intensively washed with toluene by sonication and centrifuged three cycles to remove the PCL homopolymer and other impurities. Finally, the SCMS silica-*g*-PCL ball was dried under reduced pressure at room temperature for 24 h.

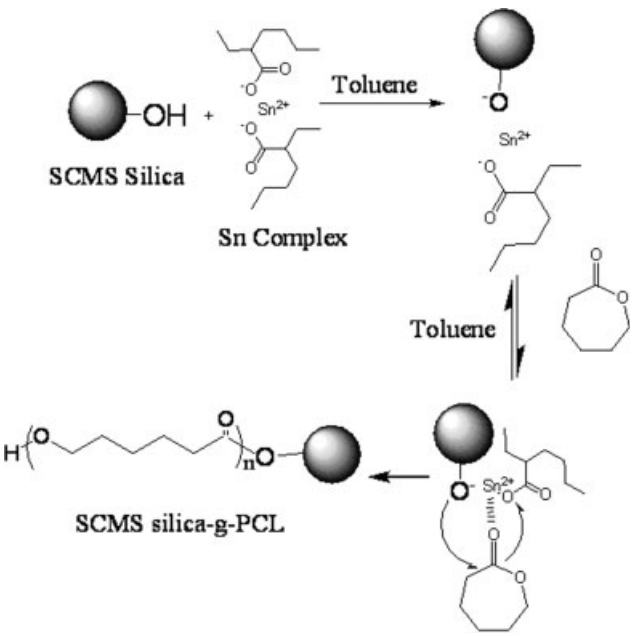
Measurements

FTIR spectra were recorded on a PerkinElmer spectrometer at a resolution of 4 cm^{-1} with a maximum of 100 scans at frequencies ranging from 400 to 4000 cm^{-1}. The samples were thoroughly mixed with KBr and pressed into pellet form. The thermal characteristics of the SCMS silica and SCMS silica-*g*-PCL were measured under a nitrogen atmosphere by differential scanning calorimetry (DSC, Q10) at a heating

rate 10°C/min and thermogravimetric analysis (TGA, 2050) at a heating rate of 20°C/min using M/s TA Instruments. The X-ray diffraction patterns of samples were obtained using a Bruker Siemens (D5000, Germany) X-ray diffractometer with a Cu Kα radiation sources (λ = 1.5418 Å). The voltage supply and current were set to 40 kV and 30 mA, respectively. The samples were exposed at a scanning rate of $2\theta = 0.4°\text{min}^{-1}$ between 2θ Values 10 and 80°. The surface morphology of the SCMS silica and SCMS silica-*g*-PCL samples was studied using scanning electron microscope (SEM, ABT-32, Topcon, Japan).

RESULTS AND DISCUSSION

Mesoporous silica spheres were synthesized based on Stober, Kaiser method, and the Giesche[22] growth process. The mesoporous particles thus obtained were almost perfectly spherical in shape and no agglomeration took place. On these particles, PCL was grafted by surface-initiated ring opening polymerization, first by treating the SCMS silica with $Sn(Oct)_2$ in toluene and then the ε-caprolactone was polymerized on SCMS silica in presence of SCMS silica-Sn(Oct) complex by coordination insertion mechanism as shown in Scheme 1. In the coordination-insertion mechanism, the initiating species is a tin alkoxide formed prior to the polymerization. Therefore the initiator can be attached to the surface that presents a hydroxyl group by the Oct-OR exchange reaction, and be transferred to the propagating polymer chain. To remove the physically adsorbed polymers, the resulting mixture was intensively washed with toluene by sonication and centrifuged, and dried under a flow of nitrogen. The SCMS Silica grafted PCL polymer chains are expected to be perpendicular to the core surface area and the specific surface area in the SCMS silica was enhanced by increasing the amount of grafting. The PCL grafted SCMS silica thus formed was characterized by FTIR, TGA, X-ray, DSC and SEM. The effect of temperature (40, 60, and 80°C) on grafting of ε-caprolactone on SCMS silica was investigated.



Scheme 1 Schematic representation of surface-initiated ring-opening polymerization of ε-caprolactone on SCMS silica surface.

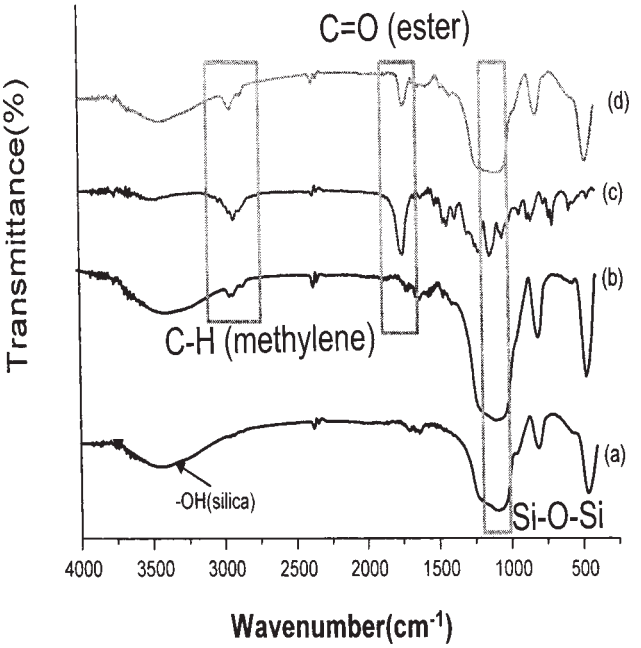


Figure 1 FTIR spectra of (a) SCMS silica ball, (b) SCMS silica-*g*-PCL (40°C), (c) SCMS silica-*g*-PCL (60°C), and (d) SCMS silica-*g*-PCL (80°C).

The FTIR spectrum of the SCMS silica (Fig. 1) showed a broad band between 3300 and 3700 cm^{-1} [Fig. 1(a)], which attributed to the primary O—H stretching of hydroxyl functional group and another broad band between 1000 and 1250 cm^{-1} attributed to the Si—O—Si stretching. SCMS Silica-*g*-PCL [Fig. 1(b)] shows new bands at 2919 cm^{-1} due to the C—H stretching, at 1740 cm^{-1} due to the C=O stretching of ester, and at 1238 cm^{-1} due to the C—O stretching of ether. The appearance of C=O ester stretching band at 1740 cm^{-1} reveals the formation of PCL grafting on the SCMS silica surface. With increase in reaction temperature from 40 to 60°C and then to 80°C [Fig. 1(b–d)], the intensity of the carbonyl stretching band at 1740 cm^{-1} and C—H stretching band at 2919 cm^{-1} enhanced indicating the increase in PCL content on SCMS silica surface.

From the TGA thermograms(Fig. 2), it is clear that SCMS silica shell does not show significant weight

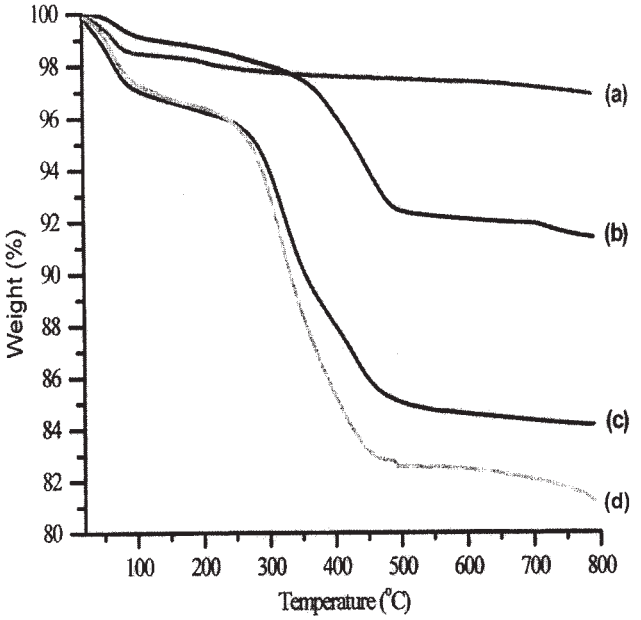


Figure 2 TGA thermogram of (a) SCMS silica ball, (b) SCMS silica-*g*-PCL (40°C), (c) SCMS silica-*g*-PCL (60°C), and (d) SCMS silica-*g*-PCL (80°C).

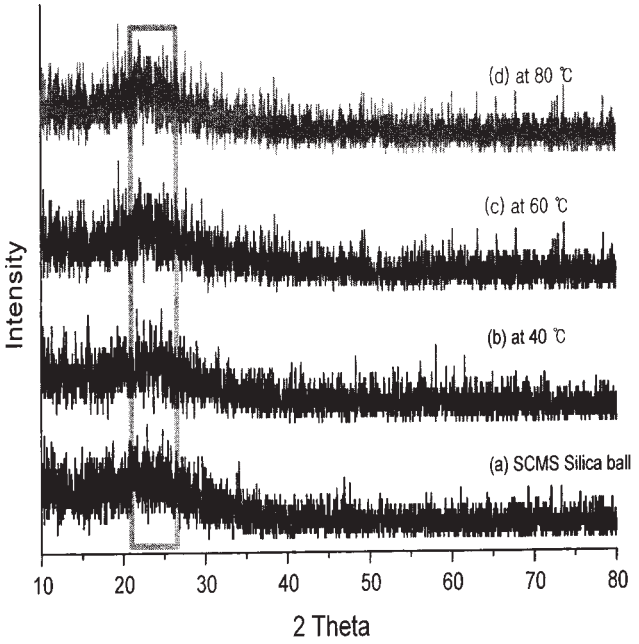


Figure 3 X-ray diffraction pattern of (a) SCMS silica ball, (b) SCMS silica-*g*-PCL (40°C), (c) SCMS silica-*g*-PCL (60°C), and (d) SCMS silica-*g*-PCL (80°C).

loss (2%) over the entire temperature range under investigation. However, the PCL grafted SCMS silica shows higher weight loss compared with neat SCMS silica, which demonstrates the formation of PCL grafting on SCMS silica surface. The percentage weight loss increased from 2 to 17% at 500°C with increase in reaction temperature from 40 to 80°C. The PCL grafting carried out at 40°C [Fig. 2(b)] shows a weight loss of 7% in the temperature range of 100–500°C, whereas the reaction carried out at 60°C [Fig. 2(c)] shows 15% weight loss and [Fig. 2(d)] the reaction carried out at 80°C shows 17% weight loss. TGA results clearly demonstrate the increase in PCL content on the SCMS silica surface with increase in reaction temperature.

The X-ray diffraction patterns of SCMS silica and SCMS silica-*g*-PCL shows only a weaker and broader hump near of $2\theta = 23^\circ$ as illustrated in Figure 3. This demonstrates that the PCL polymer grafted on SCMS silica surface does not crystallize. This may be because the PCL polymer chains grafted on the SCMS silica surface is not of high molecular weight to crystallize. However, FTIR and TGA results support the PCL grafting on the SCMS silica surface.

The DSC thermograms (Fig. 4) of SCMS silica and SCMS silica-*g*-PCL do not show any endothermic peaks in the temperature range under the investigation. This demonstrates that the polymer grafted on SCMS silica surface does not crystallize to show melting temperature (T_m). This may be because the PCL polymer chains grafted on the SCMS silica perpendicular to its surface is not of high molecular weight to crystallize to show Tm.

The SEM of SCMS silica and PCL grafted SCMS silica at different temperatures, viz. 40, 60, and 80°C are shown in Figure 5, which shows the spherical nature of the SCMS silica support was retained after grafting also. It can be seen from the SEM images

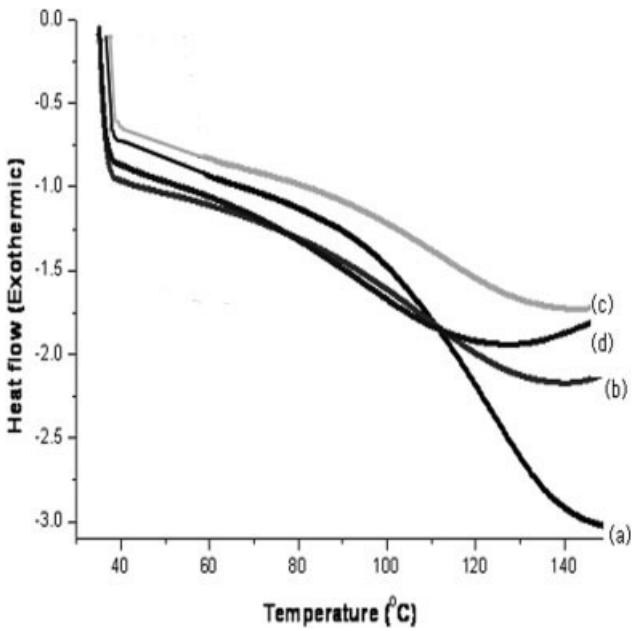


Figure 4 DSC thermogram of (a) SCMS silica ball, (b) SCMS silica-*g*-PCL (40°C), (c) SCMS silica-*g*-PCL (60°C), and (d) SCMS silica-*g*-PCL (80°C).

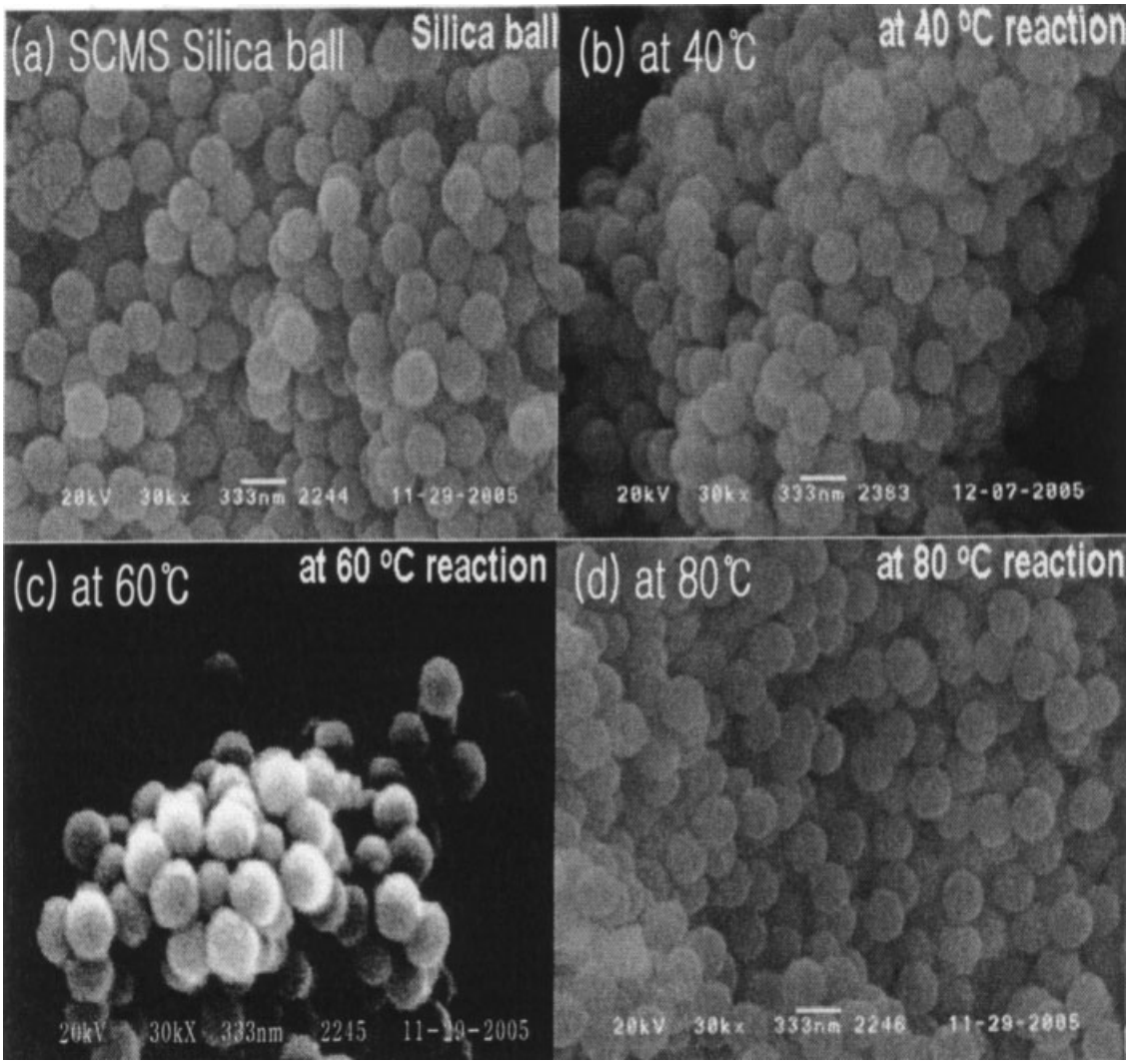


Figure 5 SEM photograph of (a) SCMS silica ball, (b) SCMS silica-*g*-PCL (40°C), (c) SCMS silica-*g*-PCL (60°C), and (d) SCMS silica-*g*-PCL (80°C).

that the resulting particles are almost perfectly spherical in shape and no agglomeration is visible, which indicates that the SCMS silica behave as a reactor to polymerization and PCL grafted on SCMS silica grown perpendicular its surface.

CONCLUSIONS

This study reports the successful grafting of PCL on SCMS silica by ring opening polymerization of ε-caprolactone in the presence of $Sn(Oct)_2$. This surface grafting was characterized by FTIR, TGA, X-ray, DSC, and SEM. The FTIR spectra demonstrate the formation of ester linkage between PCL and SCMS silica. TGA investigation shows increase in PCL content on the SCMS silica surface with increase in reaction temperature. SEM photographs clearly show the formation of PCL polymer on the SCMS silica surface without altering the spherical nature of SCMS silica sphere.

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