

A Robust Modification of SiO₂ Nanoparticles by Poly(2-hydroxyethylmethacrylate) via Surface-Initiated Atom Transfer Radical Polymerization

DUY TRINH NGUYEN¹, THUONG NHAN PHU NGUYEN¹, DUY CHINH NGUYEN¹, VAN THI THANH HO²,
MD. RAFIQUIL ISLAM³, KWON TAEK LIM³ and LONG GIANG BACH^{1,*}

¹Nguyen Tat Thanh University, 300A Nguyen Tat Thanh, District 4, Ho Chi Minh City, Vietnam

²Hochiminh University of Natural Resources and Environment, 236B Le Van Sy, Ward 1, Tan Binh District, Ho Chi Minh City, Vietnam

³Pukyong National University, Busan 608-737, Republic of Korea

*Corresponding author: Fax :+ 84 28 39404759, Tel : + 84 96 9294297; E-mail: blgiangntt@gmail.com

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An effortless and efficient method for the alteration of SiO₂ nanoparticles by poly(2-hydroxyethylmethacrylate) (PHEMA) has been developed. Initially, a strategic atom transfer radical polymerization (ATRP) initiator was anchored to SiO₂ nanoparticles surface *via* coupling reaction followed by surface-initiated atom transfer radical polymerization of HEMA successfully afforded chemically grafted PHEMA to SiO₂ nanoparticles (PHEMA-g-SiO₂). We used XPS, FT-IR and EDS analyses for confirming the covalent immobilization of PHEMA onto SiO₂ nanoparticles. TGA/DSC and zeta potentials measurements were used for determining the thermal and surface charge features of the nanocomposites, respectively.

Keywords: Surface functionalization, SiO₂ Nanoparticles, Polymer chains, Poly(2-hydroxyethylmethacrylate).

INTRODUCTION

16 There is a growing interest from modern fields such as
17 electronics, optical, biomedicine and renewable energy gener-
18 ation for development multifunctional nanomaterials. Nano-
19 structured multiphase materials could be conformed to obtain
20 multi-functionality, because various characteristics of different
21 materials can be combined to develop a wide range of fasci-
22 nating features [1-8]. Efficiency and performance of products
23 are enhanced using engineering of the interfaces in multiphase
24 materials. The combination of functional polymers and surface
25 alteration of nanoparticles is a vibrant area of current attention
26 because of their fantastic electronics, optical, magnetic and
27 catalytic features. Surface functionalization generally requires
28 appropriate synthetic methods that offer exact control over
29 material features. Several methods have been developed to modify
30 nanoparticles by polymers which significantly improved their
31 mechanical properties [9-21].

32 Nowadays, surface-initiated atom transfer radical poly-
33 merization (SI-ATRP) technique is recognized as a potential
34 and flexible methods for effective grafting of accurately identi-

fied polymers, star polymers, block copolymers, graft copolymer
and hyperbranched polymers from a variety of solid surfaces
[22-32]. The key advantage of this technique is the complete
control over the molecular weight (M_n , M_w), polydispersity
(PDI) and chain-end functionality of grafted polymer. It also
provides high graft density of polymer allowing multifuncti-
onal applications. Moreover, the ATRP is a widely practiced
method now that it does not ask to required conditions and is
accepting of functional species and contaminants that are harm-
ful to another "living" polymerization techniques.

Recently, synthesis of polymer grafted hybrid nanoparti-
cles having reactive pendant functionalities, such as hydroxyl,
carboxylic acid or epoxide groups, has gained substantial
interest as building blocks for the fabrication of advanced nano-
structured devices. Biocompatible poly(2-hydroxyethyl metha-
crylate) is an intriguing material for biology and medicine fields
as in medication carrier, dental, contact lenses, antithrombotic
equipment and soft-tissue replacement. The essential features
of poly(2-hydroxyethylmethacrylate) (PHEMA) such as
mechanical features, thermal steady, colloidal steady, moisture
content and affinity to specific biological molecules can be

56 adjusted to response with new requests. The features of PHEMA
57 can be adjusted by the combination of nanomaterials and comm-
58 anded by controlling the ingredient of inorganic or organic
59 components, nanotexture, essence of inorganic and/or organic
60 segments, *etc.* [33-37].

61 Among inorganic nanoparticles, silica spheres (SiO₂
62 nanoparticles) have excellent mechanical strength and thermal
63 stability. They are also non-toxic, easy to functionalize and can
64 be created controllably by hydrolysis of organosilicate at room
65 temperature, which makes them one of the most commonly
66 used inorganic cores. Consequently, polymers graft silica nano-
67 composites have received considerable attention in recent years
68 because of high demand for optical equipment, strengthened
69 elastomers and plastics, bioactive glass, chemical sensors,
70 biology and medicine sensors and other types [38-40].

71 In this work, the exploration of an effortless and efficient
72 procedure for precise surface alteration of SiO₂ nanoparticles
73 with poly(2-hydroxyethylmethacrylate) (PHEMA) will not
74 only reveal the surface properties of nanoparticles but also
75 open up new prospects for versatile applications. We demon-
76 strate a facile strategy for the preparation of clear identified
77 SiO₂/PHEMA nanocomposites *via* SI-ATRP. The macroini-
78 tiator (SiO₂-Br) was first prepared by one step reaction using
79 3-glycidyloxypropyltrimethoxysilane (GOTMS) and 2-bromo-
80 2-methylpropionic acid (BMPA). To obtain PHEMA-*g*-SiO₂
81 core-shell type nanocomposites, the surface of SiO₂ nano-
82 particles is modified by surface-initiated atom transfer radical
83 polymerization of 2-hydroxyethylmethacrylate (HEMA).

EXPERIMENTAL

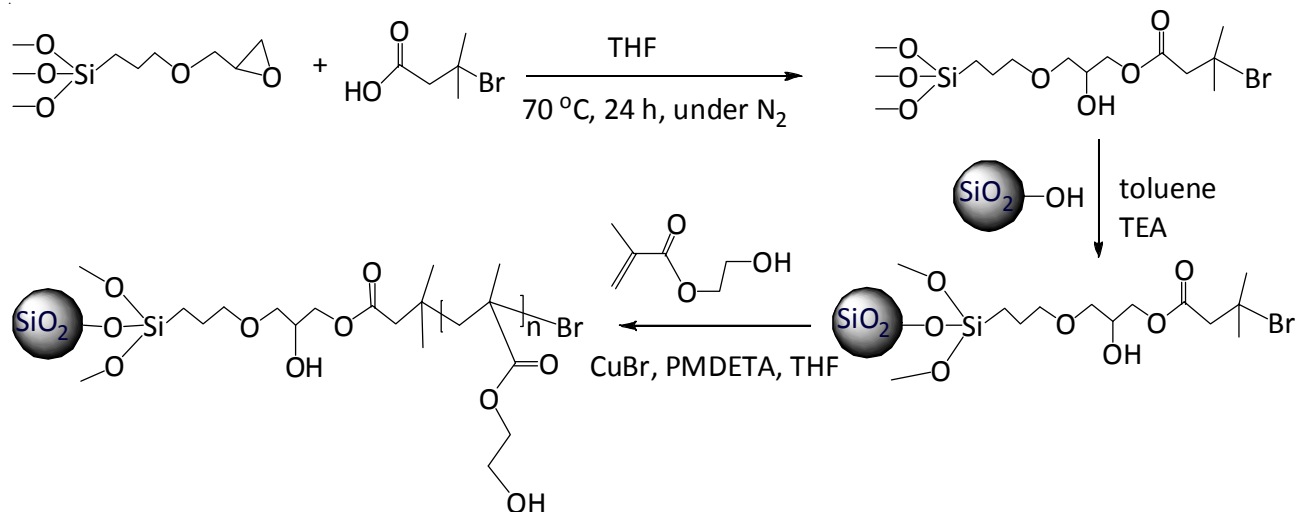
84 The SiO₂ nanoparticles with the mean size of 108 nm were
85 prepared using Stöber technique [41] with surface area of *ca.*
86 115 m²/g as measured by BET method. Purified 2-hydroxyethyl
87 methacrylate (HEMA) was produced before hand by flowing
88 a neutral alumina column to evict the inhibitor. NH₄OH (25 wt.
89 % aqueous solution), tetraoctylammonium bromide (TOAB),
90 tetraethylorthosilicate (TEOS), 3-glycidyloxypropyltrimeth-
91 oxysilane (GOTMS), 2-bromo-2-methylpropanoic acid (BMPA),
92 triethylamine (TEA), N,N,N',N',N''-pentamethyldiethylen-
93 triamine (PMDETA), CuBr, tetrahydrofuran (THF), N,N-dimethyl-
94 formamide (DMF) and all solvents were used as introduced.

Synthesis of strategic initiator (GOTMS-BMPA): 3-Glycidyl-
oxypropyltrimethoxysilane (GOTMS) (2.00 g), 2-bromo-2-
methylpropanoic acid (BMPA) (1.42 g) and THF (6 mL) were
placed in a pyrex tube. The pipe was emptied and back-filled
with nitrogen three times, then secured and held in a thermo-
statically with the oil bath at 70 °C and stirred very quickly
under N₂ atmosphere for 1 day. Lastly, all volatile materials
was removed under vacuum and marked as GOTMS-BMPA.
The ¹H NMR spectrum of GOTMS-BMPA (CDCl₃, 400 MHz,
ppm): δ = 4.15 (CH₂-CH(OH)-CH₂-O-CO-, 2H, dd); 3.67-3.71
(CH₂-CH(OH)-CH₂-O-CO-, 1H, m); 3.62 (CH₂-CH(OH)-CH₂-
O-CO-, 2H, d); 3.53 ((CH₃O)₃Si-, 9H, s); 3.45-3.47 (CH₂O-
(CH₂)₃Si-, 2H, t); 1.91 (-CH₃)₂-Br, 6H, s); 1.90 (CH₂-CH(OH)-
CH₂-O-CO-, 1H, d); 1.67 (SiCH₂CH₂CH₂O, 2H, quint); 0.65
(SiCH₂CH₂CH₂O, 2H, d).

**Synthesis of PHEMA-*g*-SiO₂ nanocomposites *via* SI-ATRP
technique**

Synthesis of SiO₂-Br macroinitiators: Dissolved 2.0 g
of SiO₂ nanoparticles in 20 mL toluene and then added 1.0 g
GOTMS-BMPA and 5 mL triethylamine (TEA) to create a
uniform suspension solution. Then, the mixture was strongly
stirred at 50 °C under N₂ flow for 1 day and subsequently, cooled
down to 35 °C and cleaned in the order with toluene and dichloro-
methane. Next, the macroinitiator SiO₂-Br was dried at 40 °C
under vacuum for 1 day.

**Synthesis of PHEMA-*g*-SiO₂ nanocomposites by SI-
ATRP method:** Mixed 2-hydroxyethylmethacrylate (HEMA,
2 g), SiO₂-Br (0.2 g), PMDETA (0.024 mL), CuBr (0.0166 g)
in 2 mL of THF using a Teflon-covered propulsion rod in a 25
mL circle bottle decorated with a restore condenser. The
mixture was removed the gas with N₂ by three freeze-pump-
thaw cycles and held in an oil tank with the temperature of 80
°C and stirred constantly. Then, the bottle was cooled to 35 °C.
Next, diethyl ether was used to precipitate the mixture and the
product was separated with centrifugation. The crude product
was cleaned and had impurities removed using THF multiple
times. Lastly, a vacuum oven was used to dry PHEMA-*g*-SiO₂
nanocomposites for a duration of 1 night at 40 °C. The synthetic
route for SI-ATRP technique to prepare PHEMA-*g*-SiO₂ using
SiO₂-Br macroinitiators is depicted in **Scheme-I**.



Scheme-I: Synthetic protocol for the preparation of PHEMA-*g*-SiO₂ nanocomposites *via* SI-ATRP technique

Characterizations: BOMEM Hartman & Braun spectrometer was used to determine FT-IR. Elemental analysis and morphological analysis of the hybrids was performed using FE-SEM photos attached with an EDX spectrometer (Hitachi JEOL- JSM-6700F). For TGA, Perkin-Elmer Pyris 1 analyzer (USA) was utilized. The DSC measurements were conducted using a Perkin Elmer calorimeter (DSC6200). Surface composition of nanocomposites was investigated using XPS (X-ray photoelectron spectroscopy) (Thermo VG Multilab 2000). GPC (gel permeation chromatography) analysis was performed using an Agilent 1200 Series equipped with PLgel 5 μ m MIXED-C columns, with N,N-dimethylformamide at 30 °C and calibration was performed by PMMA standards. The zeta potential for the surface charge properties of samples was carried out using a Zeta Plus 90 analyzer.

RESULTS AND DISCUSSION

The strategic initiators (GOTMS-BMPA) were attached on the surface of SiO₂ nanoparticles in one step through ligand-exchanging response among the -OH species on the surface of SiO₂ nanoparticles and trimethoxyliane groups of GOTMS-BMPA to produce SiO₂-Br macroinitiators. Fig. 1 showed the surface chemical composition of functionalized SiO₂ nanoparticles through EDS and XPS analyses. The EDX scan revealed the attendance of Si, O and C chemical components in SiO₂ nanoparticles as displayed in Fig. 1A. Fig. 1C showed that signals of Si, O and C elements affected the vast-scan XPS spectrum of SiO₂ nanoparticles surface. GOTMS-BMPA was attached on the surface of SiO₂ nanoparticles that causes a condensation response to form a stable initiator monolayer. Fig. 1B showed that clear signal of bromine atoms on surfaces of SiO₂-Br macroinitiators *via* EDS analysis. To assert the presence of ATRP initiators on SiO₂ nano-surfaces, SiO₂-Br macroinitiators was also analyzed XPS as shown in Fig. 1D. Expectedly, in the scan, we found that the primary peak component, nominated to O1s, and the small peak component, nominated to C1s, at the binding energy are of 533.6 and 285.0 eV, respectively. In addition to

this, peaks at the binding energy of 154.8 eV (Si2s) and 103.7 eV (Si2p) were also found. In particular, the characteristic Br3d peak as sighted at 69.2 eV, which verifies the presence of Br signals on SiO₂ nanoparticles surfaces. The EDS and XPS results confirm the success of the formation of SiO₂-Br macroinitiators.

The FT-IR was used to study the surface chemical bonding of modified SiO₂ nanoparticles. Characteristically, asymmetric stretching of Si-O-Si is associated to the absorption band, detected at 1104 cm⁻¹. The broad absorption band centered around 3431 cm⁻¹ is assigned to -OH species on the surface of SiO₂ nanoparticles (Fig. 2A). Four absorption bands at 2920 cm⁻¹ (C-H stretching of -CH₃), 2851 cm⁻¹ (C-H stretching of =CH₂), 1737 cm⁻¹ (C=O stretching) and 1114 cm⁻¹ (Si-O-Si stretching which overlapped C-O-C stretching) (Fig. 2B) indicated the interaction between GOTMS-BMPA and the surface-bound OH groups of SiO₂ nanoparticles. The surface initiated ATRP of HEMA from GOTMS-BMPA enclosed SiO₂ nanoparticles surface was performed in the attendance of CuBr/PMDETA catalyst system to give PHEMA-g-SiO₂ nanocomposites. The successful synthesis of core-shell textured PHEMA-g-SiO₂ nanocomposites was verified by respective spectral and microanalyses. Fig. 2C displayed FT-IR spectrum of PHEMA-g-SiO₂, the broad absorption band at 3647-3022 cm⁻¹ is assigned for the O-H stretching vibration and growth in intensity at 2936, 2851 cm⁻¹ is due to the C-H stretching vibration. The characteristic absorption band appeared at 1725 cm⁻¹ shows C=O stretching vibration band. The typical bands at 1225-1180 cm⁻¹ assigned for the stretching of -C-O- (in ester species). The wide absorption bands at 800-500 cm⁻¹ assigned for Si-O-Si stretching which is generally frequent in SiO₂ associated forms, and the band sighted at 1634 cm⁻¹ indicates the attendance of physically adsorbed aqua in the SiO₂ forms. FT-IR analyses suggested that PHEMA was covalently attached with SiO₂ nanoparticles *via* SI-ATRP.

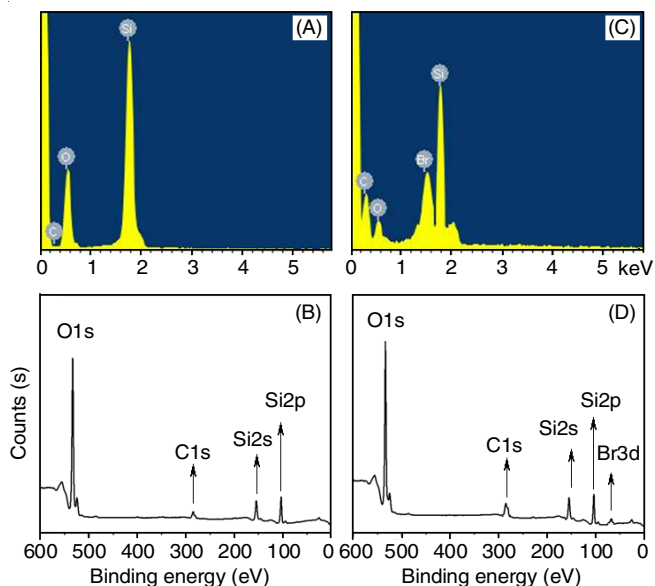


Fig. 1. (A, B) EDS and (C, D) XPS wide-scan spectra of (A, C) the SiO₂ NPs, (B, D) SiO₂-Br macroinitiators

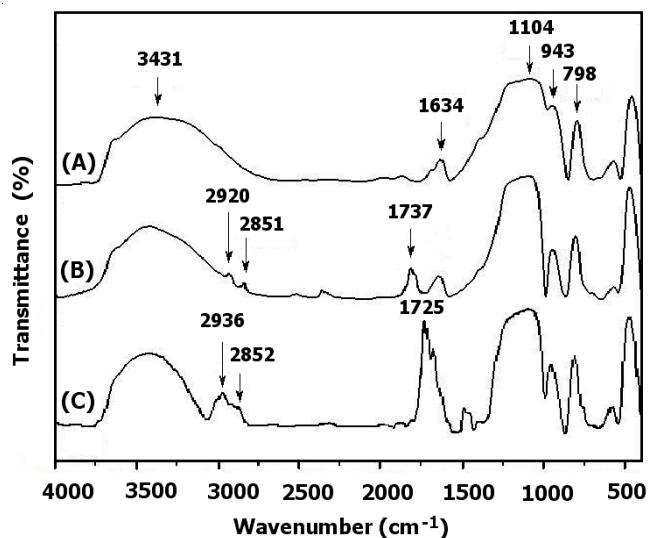


Fig. 2. FT-IR spectra of (A) SiO₂ NPs, (B) SiO₂-Br macroinitiators, (C) PHEMA-g-SiO₂ nanocomposites

Fig. 3 showed the results of thermogravimetric analysis from which the number of organic components anchored to SiO₂ nanoparticles is determined. From TGA analysis, the initial and final depropravity temperature of the samples were determined.

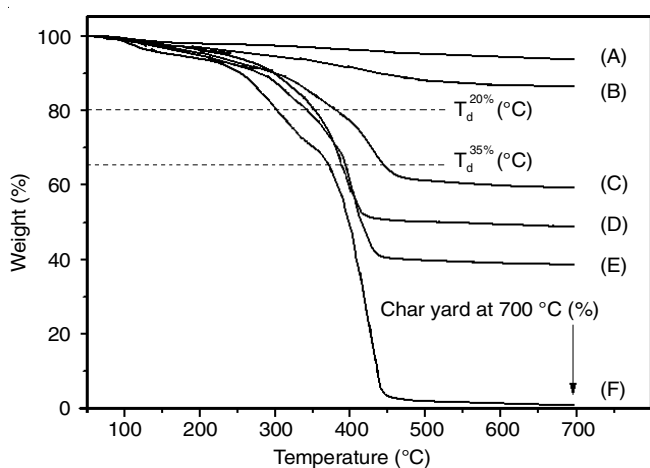


Fig. 3. TGA scans of (A) SiO₂ NPs, (B) SiO₂-Br macroinitiators, PHEMA-g-SiO₂ after polymerization for (C) 8 h, (D) 16 h, and (E) 24 h and (F) cleaved PHEMA from PHEMA-g-SiO₂ nanocomposites

208 Visually, by increasing the temperature from 50 to 700 °C, the
 209 sample of SiO₂ nanoparticles loses approximately 5.1 % of their
 210 total weight. This is due to the removal of aqua molecules
 211 adsorbed on the outer and the liberation of textured aqua caused
 212 by the bonded -OH species. Thermogravimetric analysis (Fig. 3)
 213 shows that the amount of grafted GOTMS-BMPA was calculated
 214 as to be *ca.* 10.7 %. In temperature region from 285 to
 215 430 °C, PHEMA-g-SiO₂ nanocomposites were decomposed,
 216 which is basically because of the breakdown of grafted PHEMA
 217 on SiO₂ nanoparticles. It is sighted that the weight decline of
 218 nanocomposites changed from 40.2 to 61.2 % based on the
 219 polymerization time from 8 to 24 h. The results suggested a
 220 reasonable level of functionalization of SiO₂ nanoparticles by
 221 PHEMA.

222 The condition in which SI-ATRP polymerization occurred
 223 and molecular weight of grafted PHEMA were determined
 224 by separating the grafted polymers from PHEMA-g-SiO₂ nano-
 225 composites using HF aqueous solution. The GPC analysis was
 226 performed to determine M_n and PDI of separated PHEMA. In
 227 Fig. 4, M_n and PDI of grafted PHEMA was plotted in the two
 228 vertical axes and the overall monomer conversions were displayed
 229 in the horizontal axis. The M_n of PHEMA was found to be propor-
 230 tional with increasing monomer conversion. The cleaved PHEMA

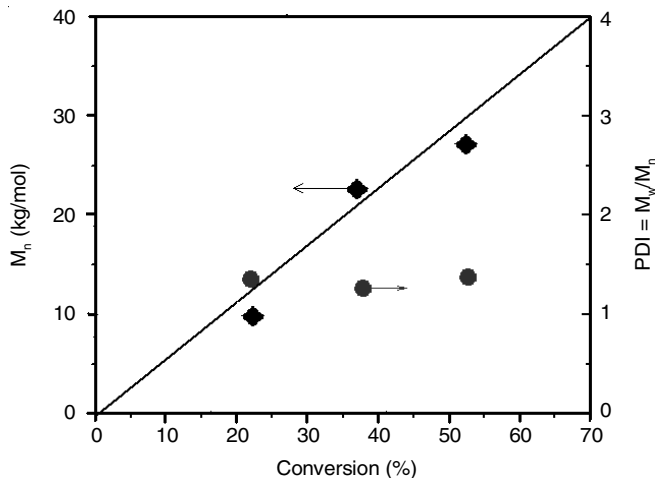


Fig. 4. M_n and PDI of the cleaved PHEMA from PHEMA-g-SiO₂ nanocomposites at different polymerization time (8, 16 and 24 h)

at polymerization time of 8, 16 and 24 h resulted in M_n of 10.5, 231
 22.7 and 27.8 kg/mol with relatively narrow PDI of 1.37, 1.26
 232 and 1.41, respectively, suggesting that SI-ATRP of HEMA
 233 from SiO₂ nanoparticles surface took place in a controlled way.

234 Thermal property of separated PHEMA and PHEMA-g-
 235 SiO₂ nanocomposites was further examined by DSC. The glass
 236 transition temperature (T_g) of cleaved PHEMA is observed at
 237 90.4 °C. On the other hand, the T_g of nanocomposites at poly-
 238 merization time of 8, 16 and 24 h were found to be 98.2, 106.6
 239 and 112.4 °C, respectively. It was observed that T_g of PHEMA-
 240 g-SiO₂ enhanced by the high grafting of PHEMA. The T_g value
 241 of grafted PHEMA is higher by *ca.* 8-20 °C than that of the
 242 equivalent neat PHEMA form (Fig. 5). The increase of T_g can
 243 be explained in such a way that the confinement of one head
 244 of PHEMA series on SiO₂ nanoparticles would limit both the
 245 motion and vibration of whole series that eventually happened
 246 in strong interaction as well as inherent high modulus of SiO₂
 247 nanoparticles resulted in increased T_g .
 248

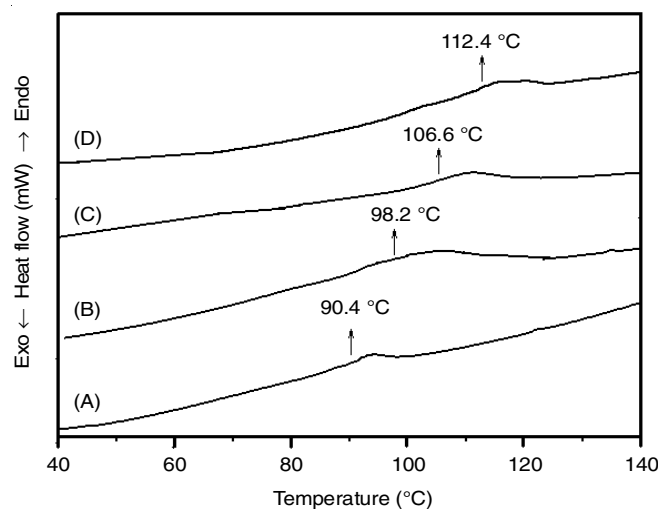


Fig. 5. DSC curves of (A) cleaved PHEMA, PHEMA-g-SiO₂ nanocomposites at polymerization time of (B) 8 h, (C) 16 h and (D) 24 h, respectively

The electrical property of particles surfaces regarding the 249
 zeta potential (ζ) is an essential factor for applications in bio- 250
 medical, industrial and environmental areas. The ζ of modified 251
 SiO₂ nanoparticles in suspension was determined using a Brook- 252
 haven Zeta Plus 90 analyzer. All the dispersions were adjusted 253
 to the desired pH with HCl (0.25 M) and NaOH (0.25 M). ζ 254
 vs pH bends for SiO₂ nanoparticles and PHEMA-g-SiO₂ nano- 255
 composites are plotted (Fig. 6). For SiO₂ nanoparticles, negative 256
 zeta voltage was found all the whole examined pH region. The 257
 surface charge density of SiO₂ nanoparticles suspensions was 258
 observed to be decreased as the pH of suspension was increased 259
 and the isoelectric point (*pI*) was reached around at pH 3.0. In 260
 opposition, ζ vs. pH bends for the PHEMA- g-SiO₂ nano- 261
 composites indicated the survival of *pI* at *ca.* pH = 6 and positive 262
 zeta voltage of situated above to + 40 mV was attained at low 263
 pH. So, this results given proof that the covalent modification 264
 of SiO₂ nanoparticles by PHEMA significantly increased the 265
 surface charge behavior of unmodified SiO₂ nanoparticles 266
 which can be used as a non-viral vector for transferring genetic 267
 materials (gene, DNA, RNA) across cellular membranes. 268

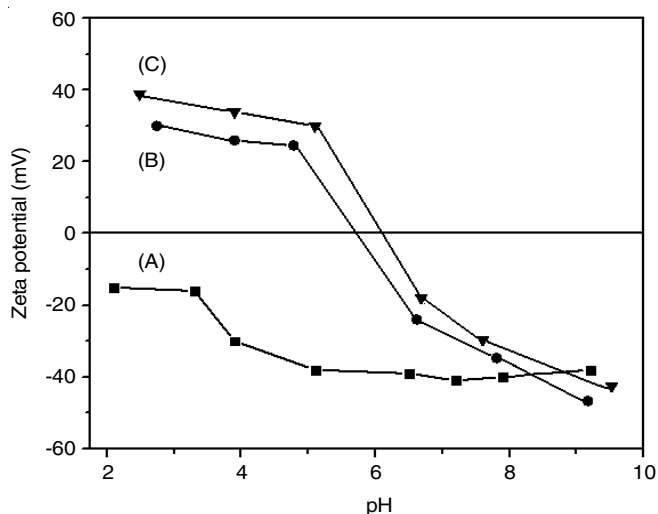


Fig. 6. Zeta potential vs. pH curves for (A) SiO₂ NPs and PHEMA-g-SiO₂ at polymerization time of (B) 8 h and (C) 24 h, respectively

269 Conclusion

270 Surface modification of SiO₂ nanoparticles by poly(2-
 271 hydroxyethylmethacrylate (PHEMA) was accomplished to
 272 afford PHEMA-g-SiO₂ nanocomposites via a facile SI-ATRP
 273 method. Following the anchoring of a sacrificial initiator GOTMS-
 274 BMPA to the surface of SiO₂ nanoparticles, chemically bonded
 275 PHEMA-g-SiO₂ nanocomposites were synthesized by SI-ATRP
 276 of 2-hydroxyethylmethacrylate (HEMA) from the surface of
 277 SiO₂ nanoparticles employing grafting from strategy as confir-
 278 med by FT-IR analyses. The thermal steady of grafted PHEMA
 279 was dramatically improved compared to pure PHEMA as
 280 suggested by TGA and DSC studies. The controlled nature of
 281 polymerization was evidenced by the linear increase of M_n of
 282 the separated PHEMA from PHEMA-g-TiO₂ nanocompo-
 283 sites with monomer conversion and the relatively low PDI (< 1.5).
 284 The zeta potential of functionalized SiO₂ nanoparticles
 285 indicated that surface modification by PHEMA using SI-ATRP
 286 is a fantastic strategy for manipulating surface electrostatic
 287 character of SiO₂ nanoparticles. This facile chemical strategy
 288 holds a great promise for surface engineering of nanoparticles
 289 in material science and nanotechnology to devise a cascade of
 290 promising materials for diverse applications.

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CONFLICT OF INTEREST

293 The authors declare that there is no conflict of interests
 294 regarding the publication of this article.

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