Electronic Supplementary Material (ESI) for Polymer Chemistry.

RAFT mediated one-pot synthesis of glycopolymer particles with tunable core-shell morphology

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Supporting information

Experimental section

Source of Materials

Styrene (St) (Sisco Chem., India) was vacuum distilled prior to use. 4,4'-Azobis (4-cyanopentanoicacid) (ACP, Sigma-Aldrich) was purified by recrystallization from methanol. HPLC grade water (Fisher Scientific) and AR grade ethanol (Changshu Yangyuan Chemical, China) were used as a solvent for all the polymerization reactions. All the other chemicals were reagent grade unless otherwise mentioned.

Synthesis of Benzylsulfanylthiocarbonylsufanylpropionic acid (BSPA) RAFT agent

Benzylsulfanylthiocarbonylsufanylpropionic acid (BSPA) RAFT agent was synthesized using the previously reported method.[1, 2] Briefly, potassium hydroxide (3.366g, 60 mmol) was added in distilled water (30 mL) followed by the addition of mercaptopropionic acid (2.614g, 30mmol) in a dried 250 mL round bottom flask. Then carbon disulphide (3.988g, 66 mmol) was added with an addition funnel at a rate of 0.1ml/min, formation of an orange colour solution was observed and it was stirred for 5hours at room temperature. Then benzyl bromide (5.131g, 30 mmol) was added and the reaction mixture was stirred at 80°C for 12 hours. After completion of the reaction, it was cooled to room temperature followed by the addition of chloroform (30 mL) and then the reaction mixture was acidified with aqueous hydrochloric acid (1N) until the organic layer become yellow. The water phase was extracted with chloroform (30 mL) twice and dried over anhydrous magnesium sulphate overnight. After the evaporation of the solvent, the remaining product was purified by silica gel column chromatography with a 7:3 hexane/ethyl acetate mixture as an eluent. Then the product was recrystallized from 7:3 hexane/ethyl acetate and dried in vacuum overnight. Yellow colour solid (6.69g, 82%) was obtained and characterized by ^{1}H NMR as presented in Fig.S1 (A).

Characterization techniques

The emulsions formed after the reaction were dialyzed with a 3.5 KDa Spectra Pro dialysis membrane to remove any unreacted monomers, initiators and RAFT reagent from the emulsions for further characterization. A portion of the emulsion was evaporated on a clean glass bottle at room temperature for 48 hours and the glycopolymer nanoparticle powder was collected and used for ^{1}H NMR, TGA, DSC, UV-Vis and GPC analysis.

^{1}H NMR spectroscopic analysis of glycopolymer was performed using a Bruker AV 400 MHZ NMR spectrometer at room temperature. To prepare the sample, 10 mg of powdered glycopolymer sample was dissolved in a 50/50 mixture of $CDCl_3$ and DMSO-d_6 to perform the NMR experiment.

UV-Vis Spectroscopic analyses were carried out in absorbance mode on a carry 100Bio UV-Vis spectrophotometer to check the presence of sugar moiety on the prepared glycopolymer nanoparticles and were conducted by dissolving glycopolymer powder in 50% DMSO in $CHCl_3$.

Field Emission Scanning Electron Microscopy (FESEM) images were taken from Carl Zeiss Ultra-55 using EHT detector at 5 kV voltage. Sample preparation was done by placing the diluted colloidal juice on a glass plate, then dried at room temperature and gold coated before imaging in FESEM.

Transmission electron microscopy (TEM) studies were conducted on FEI (Technai Model No. 2083) TEM machine at an accelerating voltage of 200 kV. The samples were prepared by placing highly diluted colloidal juice on carbon coated copper (200 mesh) grids.

Molecular weights and polydispersity index (PDI) of glycopolymers were determined by Gel Permeation Chromatography (GPC) using polystyrene standards and eluted in DMAc at flow rate of 0.4 mL/min at 25 °C on a GPC (Waters 515 HPLC) fitted with Waters 2414 refractive index detector and using Styragel HR 4E DMF column.

Thermo gravimetric analysis (TGA) of glyconanoparticles was carried out on TG-DTA, (Netzsch STA 409PC) from 30 to 800 ^{o}C with a scanning rate of 10 °C/min in presence of nitrogen flow.

A differential scanning calorimetry (DSC) instrument (Pyris Diamond DSC, Perkin Elmer) was used to measure the glass transition temperature (T_g) and melting temperature (T_m) of the powder sample by scanning the sample from 20 to 150 °C with a scanning rate of 5 °C min^{-1}. Before scanning, the DSC was calibrated using In and Zn.

The zeta potential measurements of synthesized glyconanoparticles were carried out on a Zetasizer (Nano ZS90) operating at 4mW He-Ne laser with 633nm wavelength at room temperature.

Confocal Raman microscopic analysis was carried on Alpha300 RA microscope (WITec GmbH, Ulm, Germany) equipped with a frequency NdYAG laser (λ = 532 nm) and a 100X (NA = 0.9) air objective.

The wide angle X-ray diffraction (WXRD) patterns of the samples were collected from a Bruker D8 Advance X-ray diffract meter (Bruker-AXS, Karlsruhe, Germany) in the Bragg–Brentano geometry using Cu Kα radiation (k = 1.5406 Å) at 40 kV and 30 mA. Diffraction patterns were collected over the 2θ range 5–50° at a scan rate of 1 min^{-1}with a time per step 0.5 s. The sample was well ground to make powder and mounted on a flat sample holder. The powder sample manually sieved on the sample holder in order to mitigate the effects of preferred orientation.

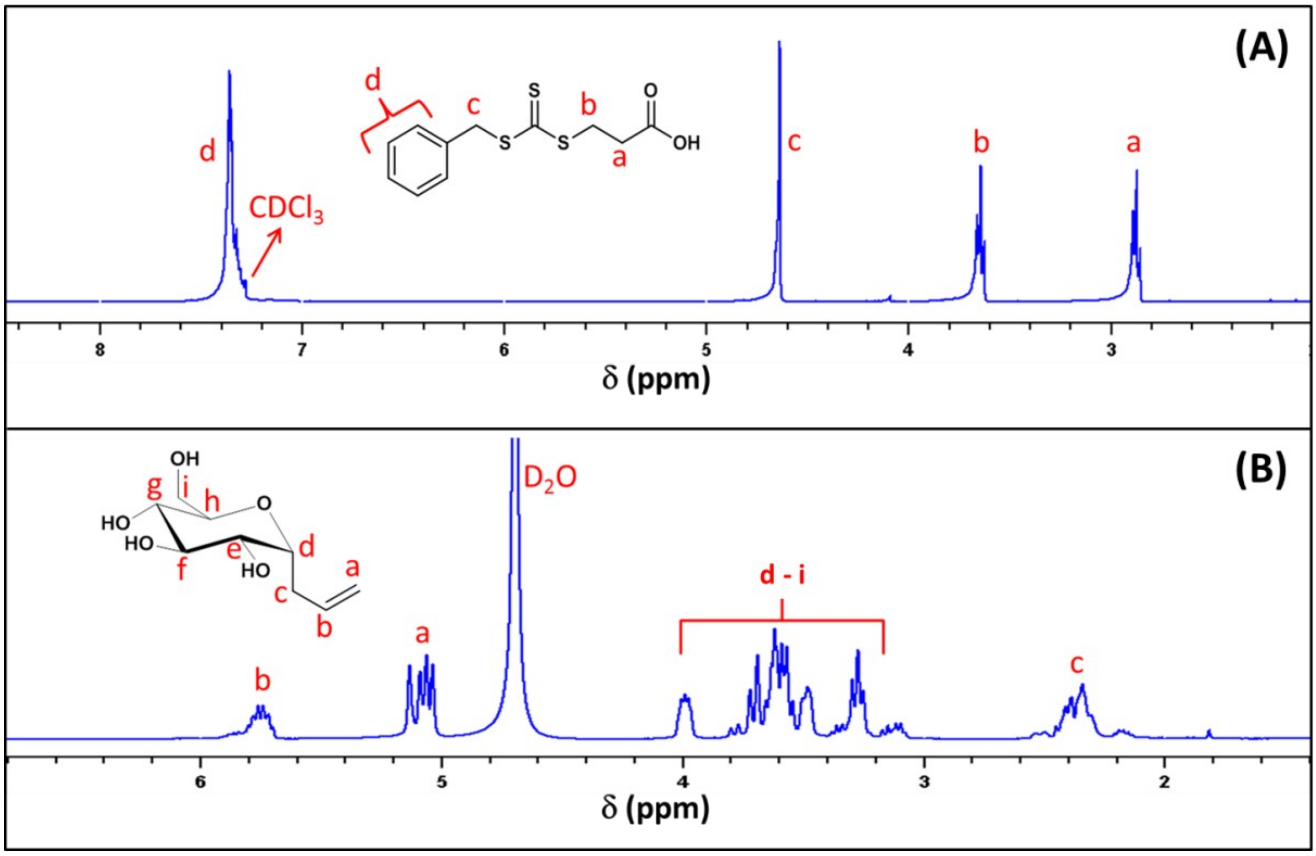

Fig.S1 [1]H NMR spectra of (A) BSPA RAFT agent and (B) glycomonomer (sugar).

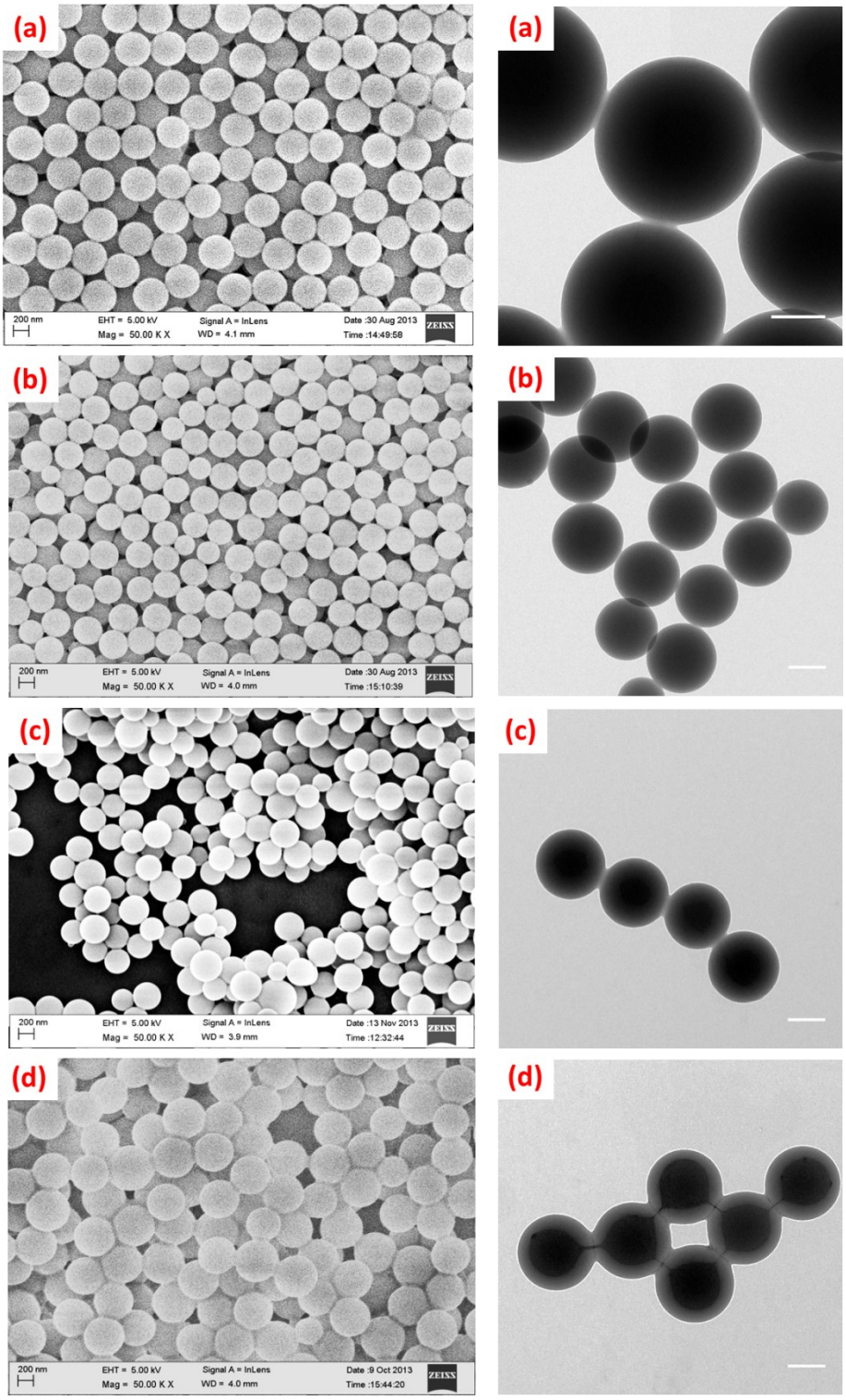

Fig.S2 FESEM (left panel) and TEM (right panel) images glyconanoparticles with a macro sugar chain length of 2K with a variation of sugar content (a) 2 wt%, (b) 5 wt%, (c) 7.5 wt% and (d) 10 wt% in the reaction. The scale bar for TEM images is 200 nm.

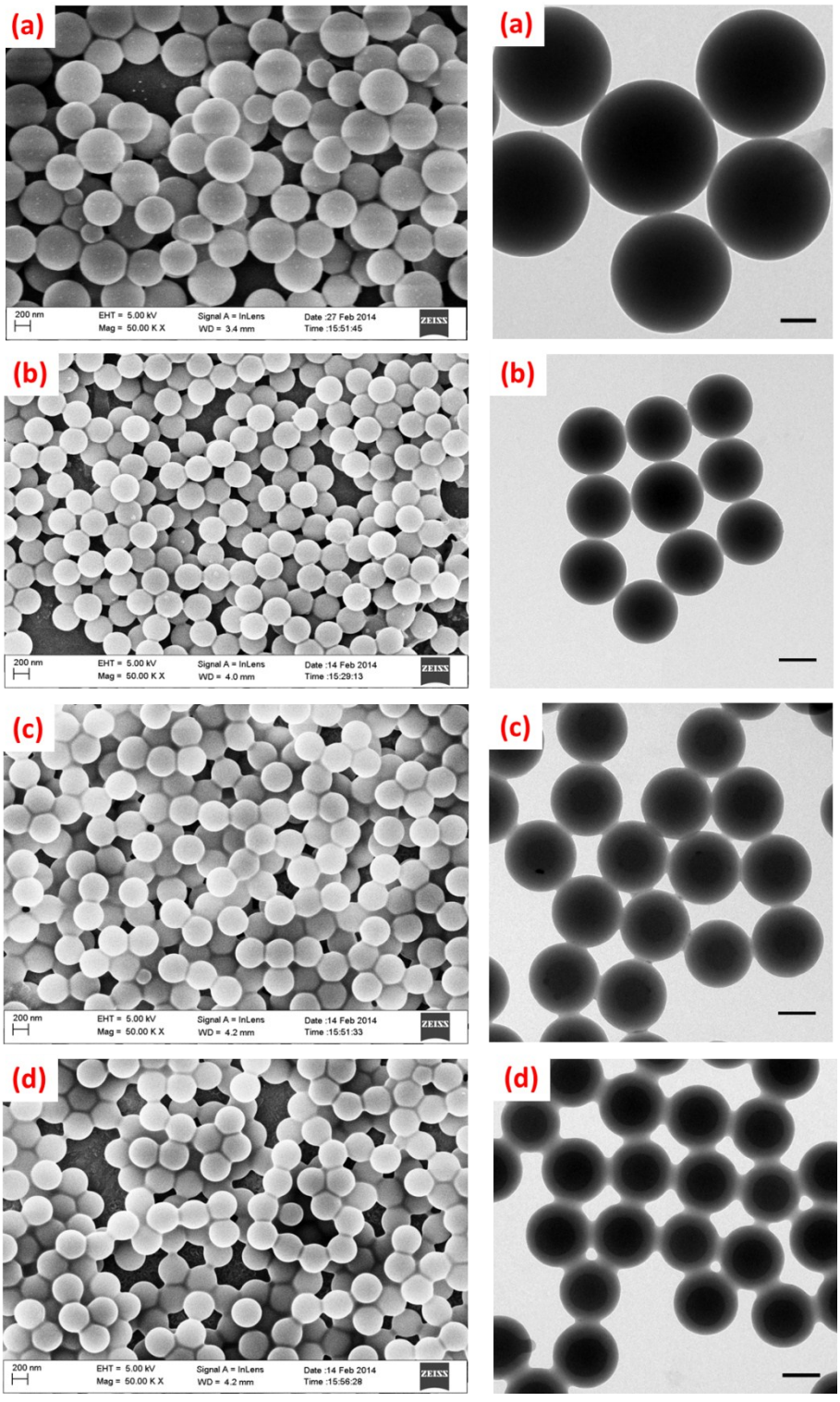

Fig.S3 FESEM (left panel) and TEM (right panel) images glyconanoparticles with a macro sugar chain length of 5K with a variation of sugar content (a) 2 wt%, (b) 5 wt%, (c) 7.5 wt% and (d) 10 wt% in the reaction. The scale bar for TEM images is 200 nm.

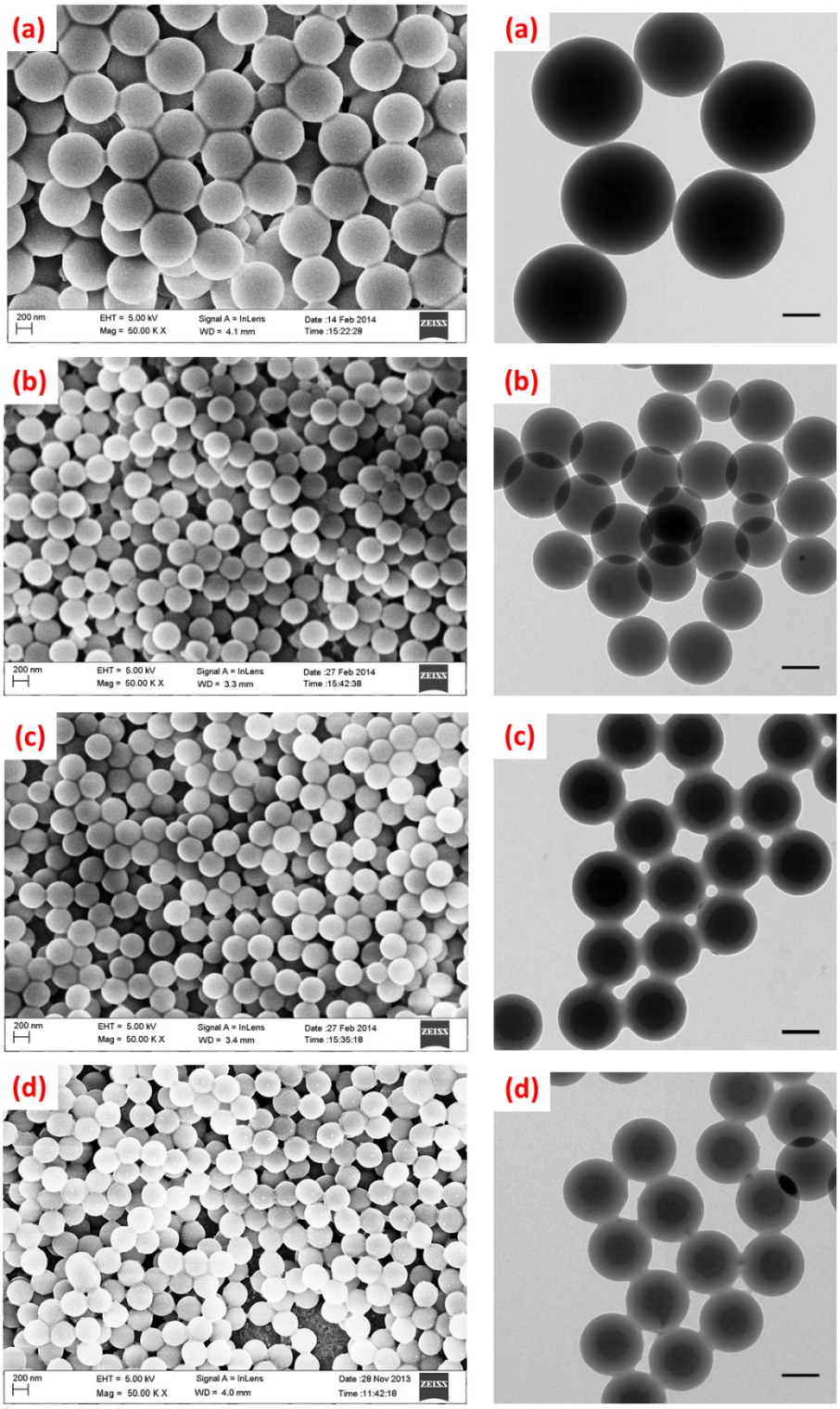

Fig.S4 FESEM (left panel) and TEM (right panel) images glyconanoparticles with a macro sugar chain length of 8K with a variation of sugar content (a) 2 wt%, (b) 5 wt%, (c) 7.5 wt% and (d) 10 wt% in the reaction. The scale bar for TEM images is 200 nm.

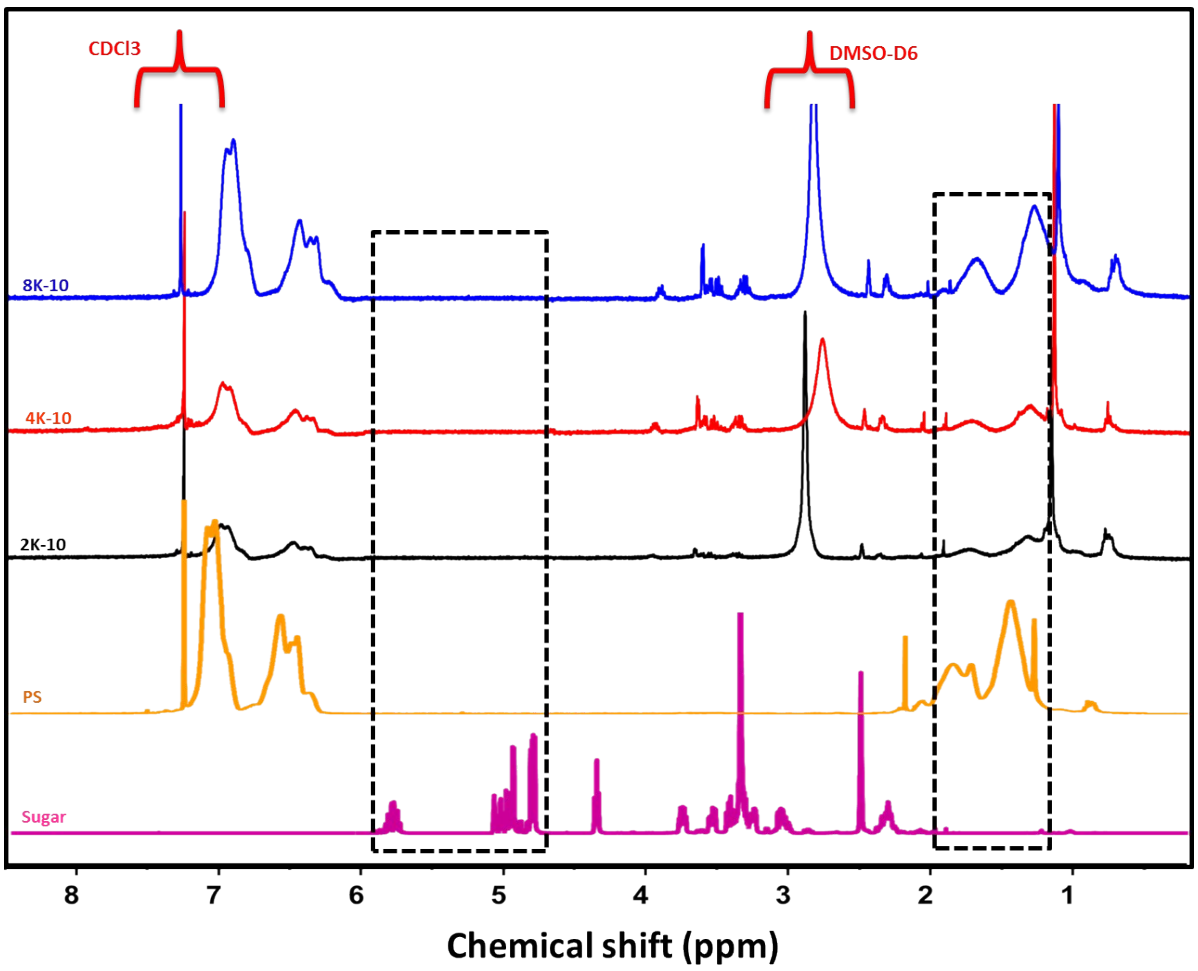

Fig.S5 ^{1}H NMR spectra of PS-glycopolymers prepared using 10 wt% sugar with respect to main monomer styrene by varying macro sugar chain length (2K,4K and 8K) along with pure sugar and polystyrene (PS).

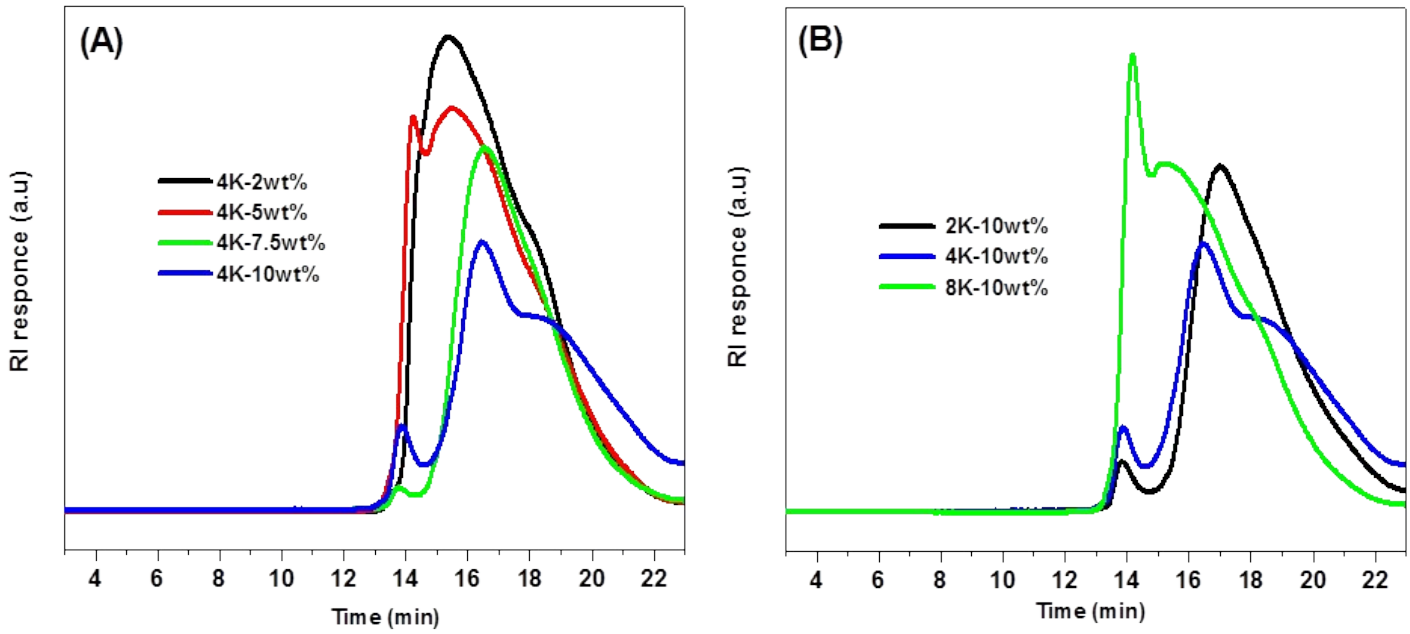

Fig.S6 GPC traces of PS-glycopolymers synthesized with (A) macro sugar chain length of 4K and variation of sugar content 2 wt%, 5 wt%, 7.5 wt% and 10 wt% with respect to styrene and (B) 10 wt% sugar with respect to monomer styrene by varying macro-sugar chain length (2K,4K and 8K).

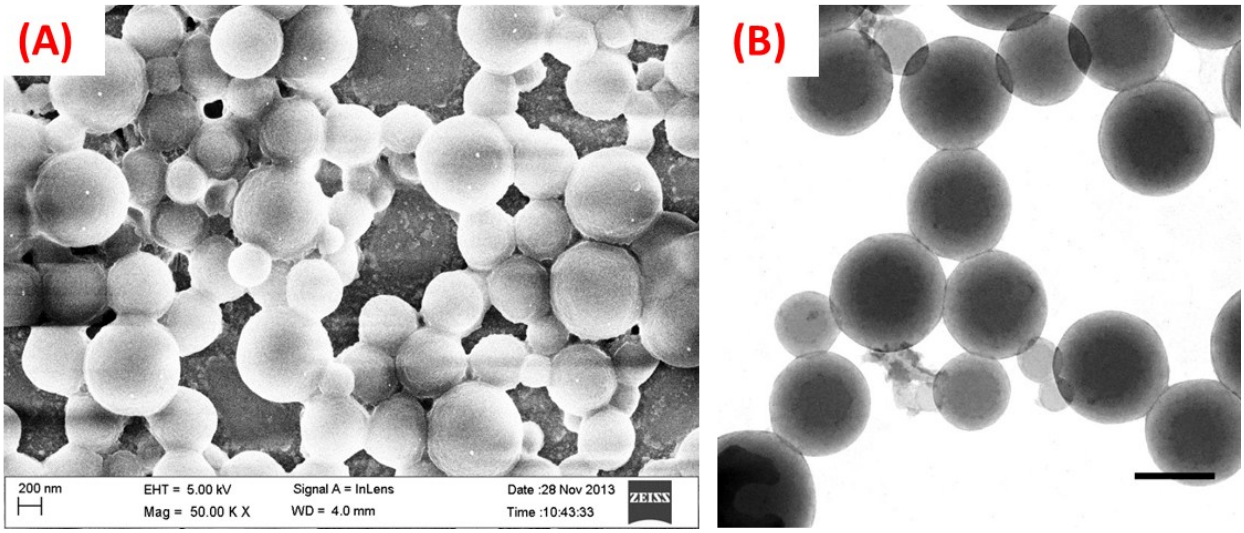

Fig.S7 FESEM (A), TEM (B) images of glycopolymers prepared using 10 wt% of sugar (as in the case of 4K-10 wt%) but without any added RAFT reagent. TEM scale bar is 200 nm.

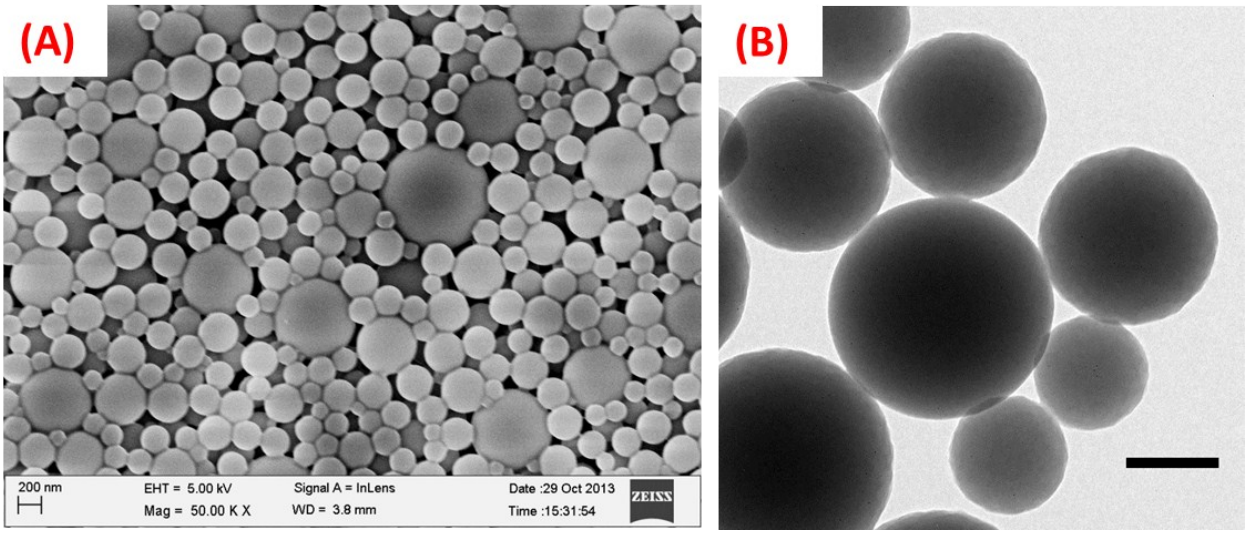

Fig.S8 FESEM (A), TEM (B) images of polymers prepared without RAFT reagent and sugar in the reaction. TEM scale bar is 200 nm.

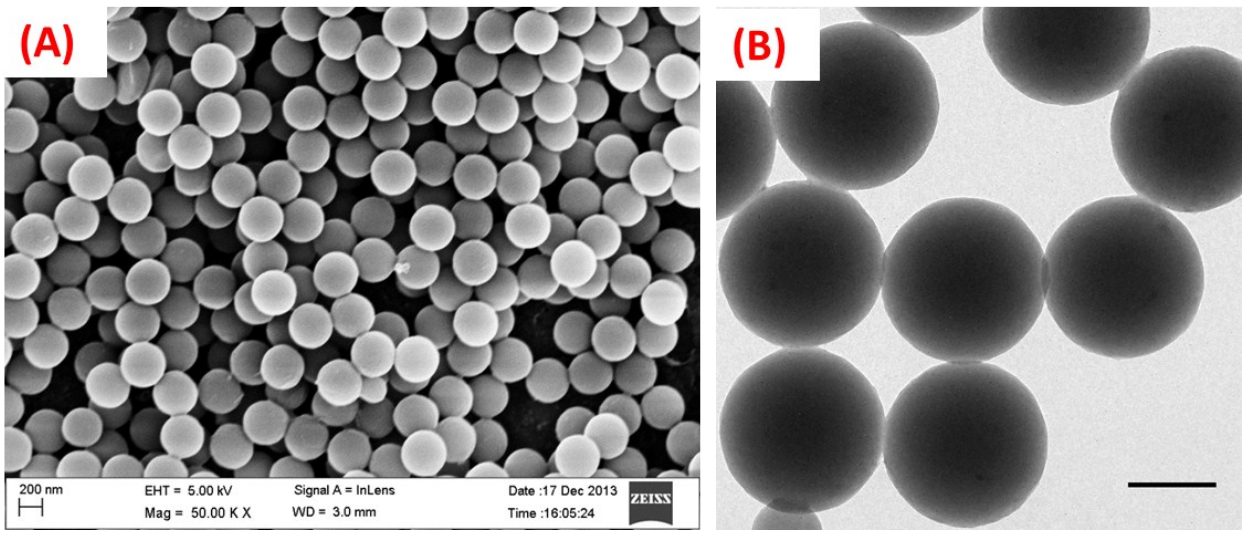

Fig.S9 FESEM (A), TEM (B) images of glycopolymers prepared by adding RAFT agent (amount is equal to 4K-10 wt %) but without any addition of sugar monomer. TEM scale bar is 200 nm.

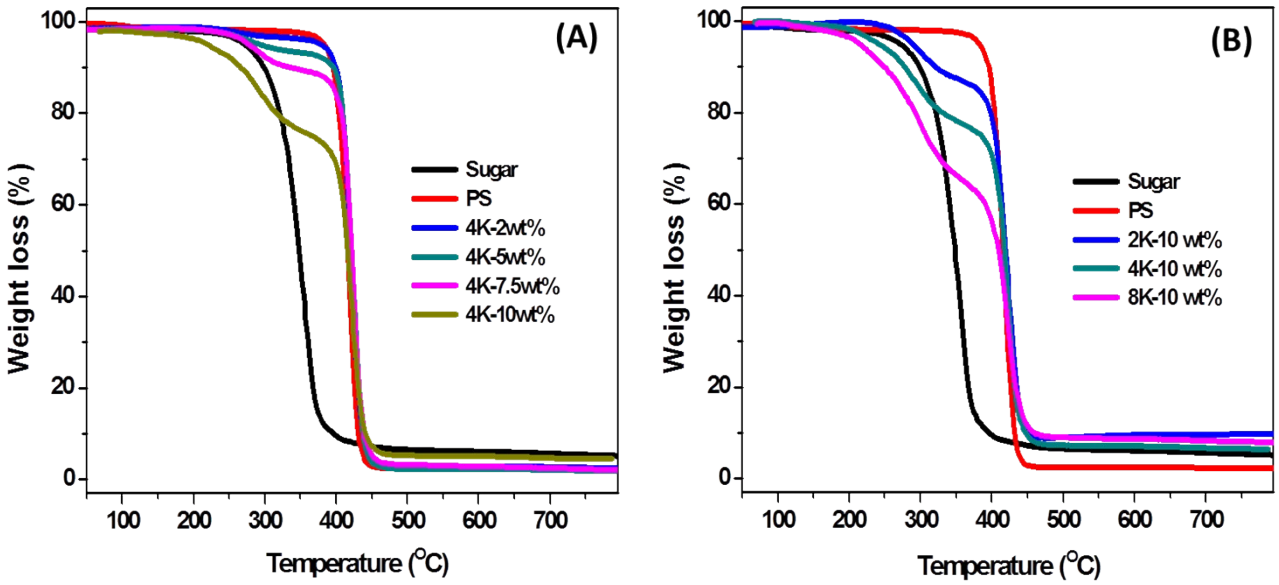

Fig.S10 TGA thermograms of PS-glycopolymers prepared using (A) macro sugar chain length of 4K by varying sugar wt% and (B) 10 wt% sugar with respect to monomer styrene by varying macro sugar chain length (2K,4K and 8K) along with pure sugar and polystyrene.

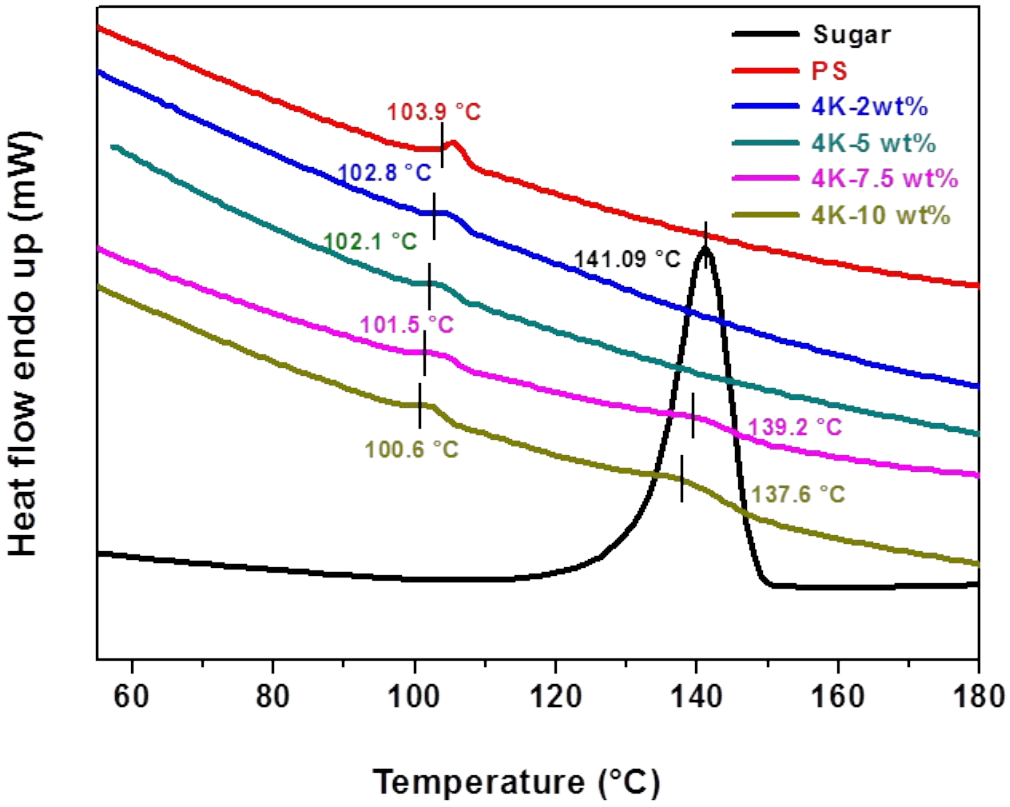

Fig.S11 DSC thermograms of PS-glycopolymers prepared using macro sugar chain length of 4K by varying sugar wt%. Also DSC of sugar monomer and PS are shown in the figure for comparison.

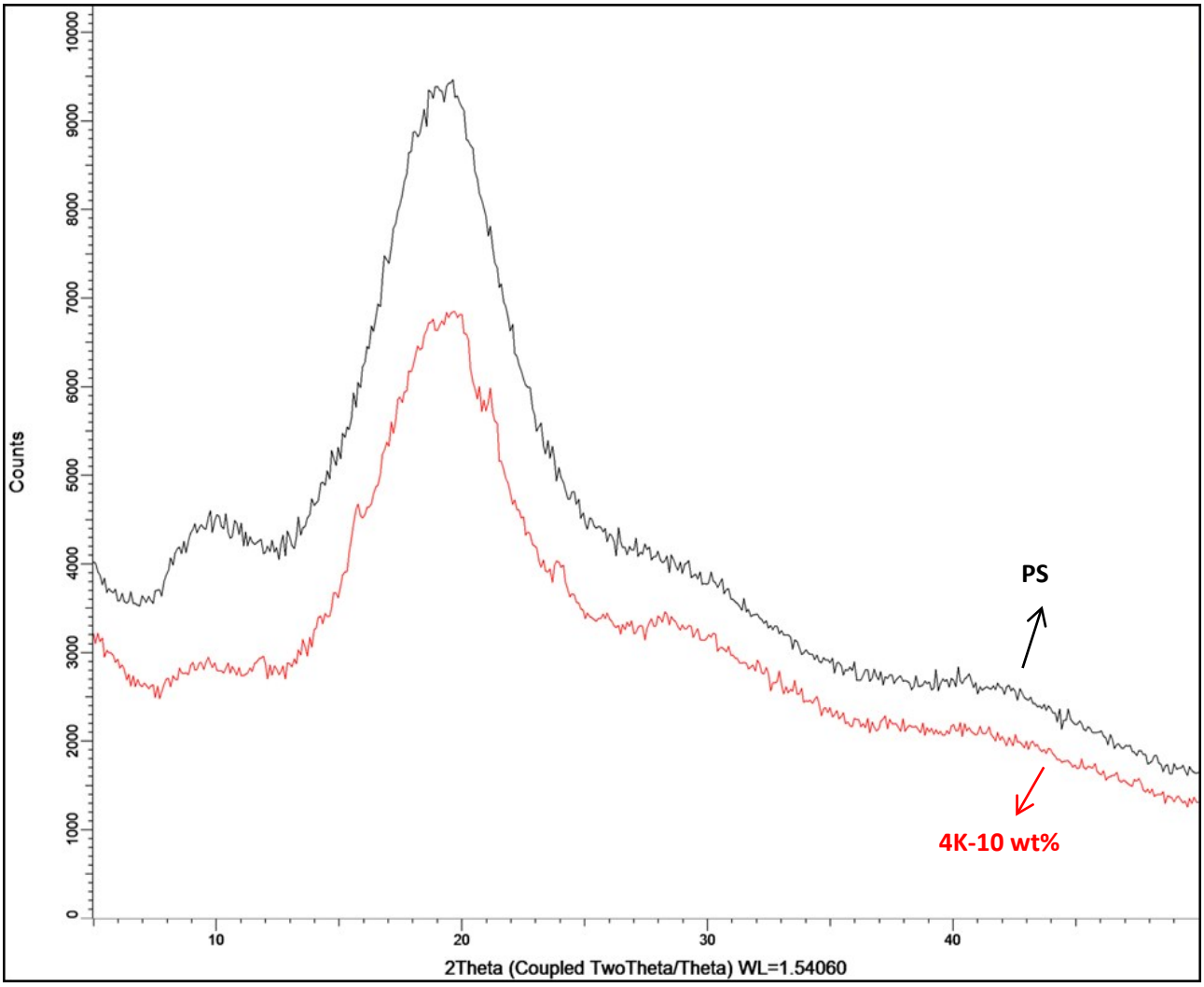

Fig. S12. WXRD patterns of PS and PS-glycopolymer prepared using macro sugar chain length of 4K with 10 wt% sugar monomer.

References

1. S. Bhattacharjee and D. Bong, *J. Polym. Environ.*, 2011, 19, 2103-2208.

2. C. Boyer, V. Bulmus and T. P. Davis, *Macromol. Rapid Commun.*, 2009, 30, 493-497.