Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information to

ATRP mediated encapsulation of Gibbsite: fixation of the morphology by using a cross-linker

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Experimental

Materials

Methyl methacrylate (MMA, Aldrich, 99%), butyl acrylate (BA, Aldrich, 99%), ethylene glycol dimethacrylate (EGDMA, Aldrich, 98%) were purified by passing them through a column packed with inhibitor removal. $CuBr_2$ (99.999%, Aldrich), ascorbic acid (99%, Aldrich), tris(2-pyridylmethyl)amine (TPMA, 99%, Aldrich), were used as received.

Characterisation

The particle size distribution and zeta-potential (ζ) were determined at 23°C using a Malvern Zetasizer Nano ZS instrument. The ζ-potential was calculated from the electrophoretic mobility (μ) using the Smoluchowski relationship, $\zeta = \eta\mu/\varepsilon$, with $\kappa a >> 1$ (where η is the dynamic viscosity, ε is the dielectric constant of the medium. κ and a are the reciprocal value of the "thickness of the electric bilayer" and particle radius, respectively).

Cryogenic transmission electron microscopy (cryo-TEM) measurements were conducted on a FEI Tecnai 20, type Sphera TEM instrument (with a LaB_6 filament, operating voltage = 200kV). The sample vitrification procedure was performed using an automated vitrification robot (FEI Vitrobot Mark III). A 3µl sample was applied to a Quantifoil grid (R 2/2, Quantifoil Micro Tools GmbH; freshly glow discharged for 40 seconds just prior to use) within the environmental chamber of the Vitrobot and the excess liquid was blotted away. The thin film thus formed was shot into melting ethane. The grid containing the vitrified film was immediately transferred to a cryoholder (Gatan 626) and observed under low dose conditions at -170°C.

Synthesis of polymer-Gibbsite nanocomposites

Gibbsite was synthesised according to the method described by Wierenga *et al.*[1] The aqueous dispersion (1 wt%) of Gibbsite had a ζ-potential of +40 mV and a *Z*-average diameter of 100 nm with a poly value of 0.14 at pH ≈ 7.[2] The ATRP macroinitiator (BA_4-co-AA_8) with $M_n = 1.4 \times 10^3$g mol^{-1} and $Đ = 1.15$ was synthesised as reported previously.[2] The adsorption procedure of the ATRP macroinitiator on Gibbsite platelets was performed as described previously.[2] The amount of macroinitiator was equal to 300 mg per g of Gibbsite and was used for further encapsulation studies, since the same amount was used before.[2]

Polymer encapsulated Gibbsite nanoparticles were synthesized by ARGET ATRP starved feed emulsion polymerization.[2] The starting reaction mixture was the same in all three profiles. Briefly, 1.4 mL of a 10 mM aqueous stock solution of ATRP macroinitiator and 30 mL of DDI water were transferred into a 50 mL three neck flask after which 2 mL of Gibbsite dispersion (1 wt%) was added dropwise at a rate of 1 mL min^{-1} using a syringe pump NE-1000 under constant stirring at room temperature. The resulting dispersion was then sonicated for 1.5 min using Vibracell tip sonicator at 30% amplitude. 2 mL of copper catalyst (10.9×10^{-5} mmol [$CuBr_2$]:[TPMA]=1:8) was added and the reaction mixture was purged with argon for 30 minutes after which the flask was heated to 70°C. At this point continuous feeding of 5 mL of 22.2×10^{-6} M aqueous ascorbic acid solution at a rate of 9 mg min^{-1} began using a syringe pump NE-1000.

Profile I: At the same time 0.45 g of deoxygenated EGDMA was injected into the reaction mixture. After two hours 4.5 g of deoxygenated monomer mixture (MMA:BA=10:1 w/w) was fed at a rate 9 mg min^{-1} using the same syringe pump. After the completion of monomer and ascorbic acid addition, the flask was kept stirring at 70°C for another two hours.

Profile II: At the same time 0.45 g of deoxygenated EGDMA at the same rate was fed using syringe pump NE-1000. After the cross-linker addition was finished 4.5 g of deoxygenated monomer mixture (MMA:BA=10:1 w/w) was fed at a rate 9 mg min^{-1} using the same syringe pump. After the completion of monomer and ascorbic acid addition, the flask was kept stirring at 70°C for another two hours.

Profile III: At the same time 4.95 g of deoxygenated mixture of monomer (MMA:BA = 10:1 w/w) and EGDMA (10 wt% based on overall monomer content) at the same rate was fed using syringe pump NE-1000. After the completion of monomer and ascorbic acid addition, the flask was kept stirring at 70°C for another two hours.

Effect of EGDMA addition

Effect of EGDMA addition profile on colloidal stability was analysed by measuring zeta-potential during the reaction (Fig. S1).

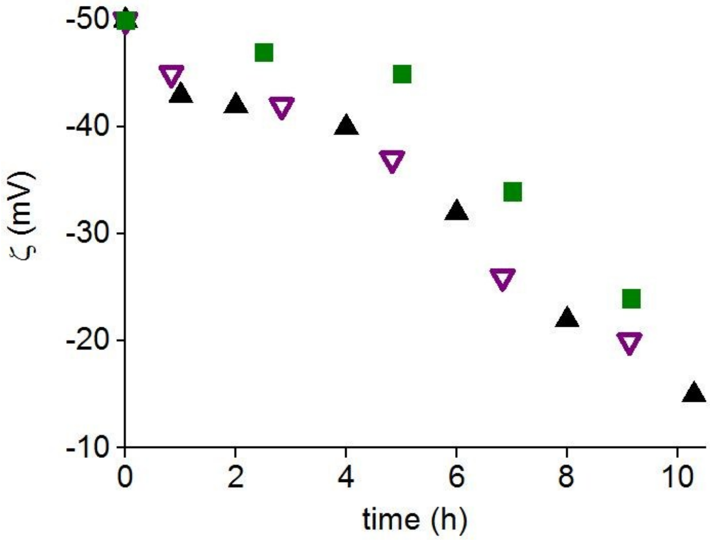
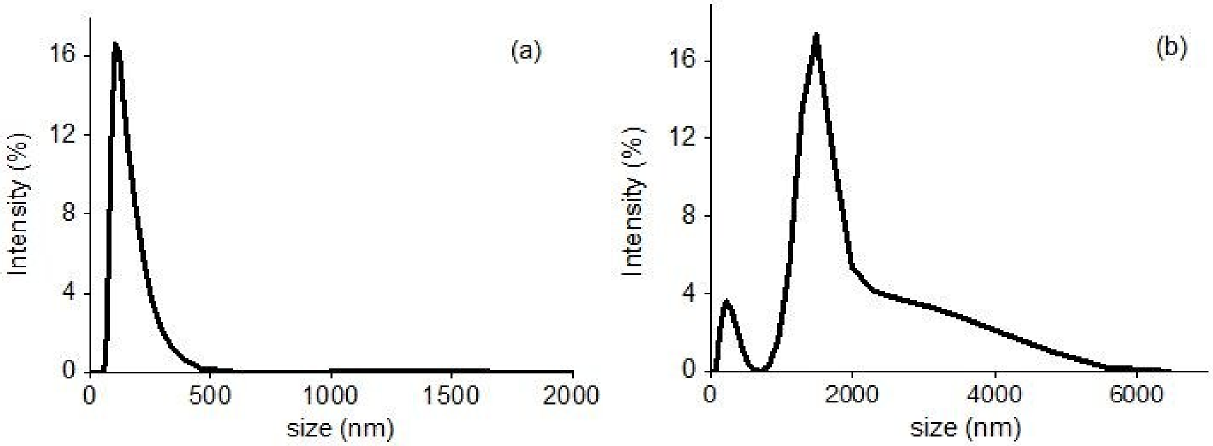


Fig. S1 Evolution of the ζ-potential obtained using different addition profiles of EGDMA: (□) profile *I*, (♦) profile *II* and (■) profile *III*. Reaction conditions: V_{water} = 30 mL, T = 70°C, 6 mg of ATRP macroinitiator and 20 mg of Gibbsite per mL, [ascorbic acid]$_0$ = 2.6×10^{-6} M, [Cu^{2+}]$_0$ = 2.6×10^{-6} M, MMA : BA = 10 : 1 w/w, feeding rates of ascorbic acid, MMA/BA and EGDMA were 9 mg min^{-1}. The final product consists of 247.5 g polymer per g Gibbsite.

Diameter distribution curves by number, volumes, and intensity were recorded for obtained polymer-Gibbsite nanocomposites by using profile *I* (Fig. S2) and *II* (Fig. S3).



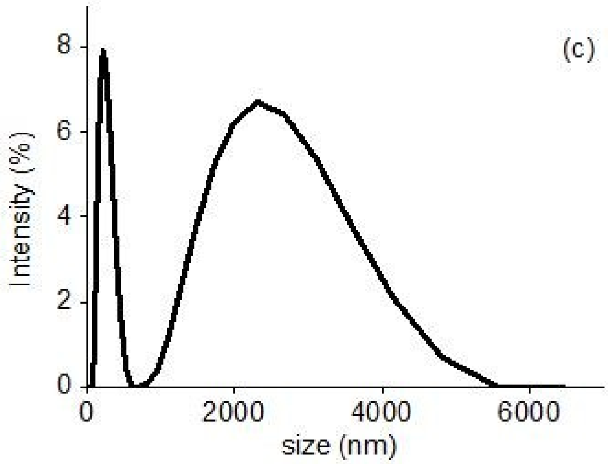


Fig. S2 Diameter distribution curves by number (a), volumes (b), and intensity (c) of polymer-Gibbsite latex particles obtained using profile *I*. Other conditions as in Fig. S1.

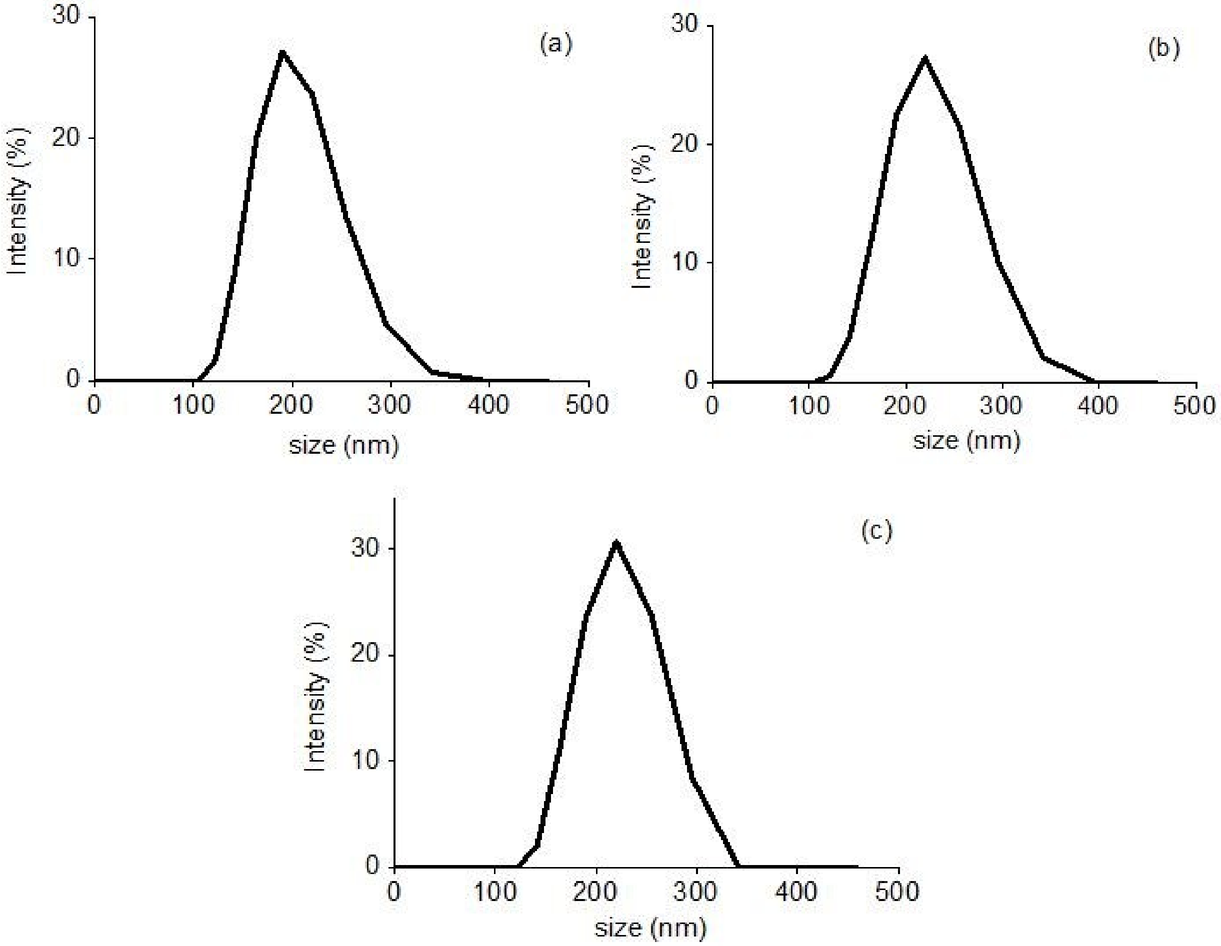
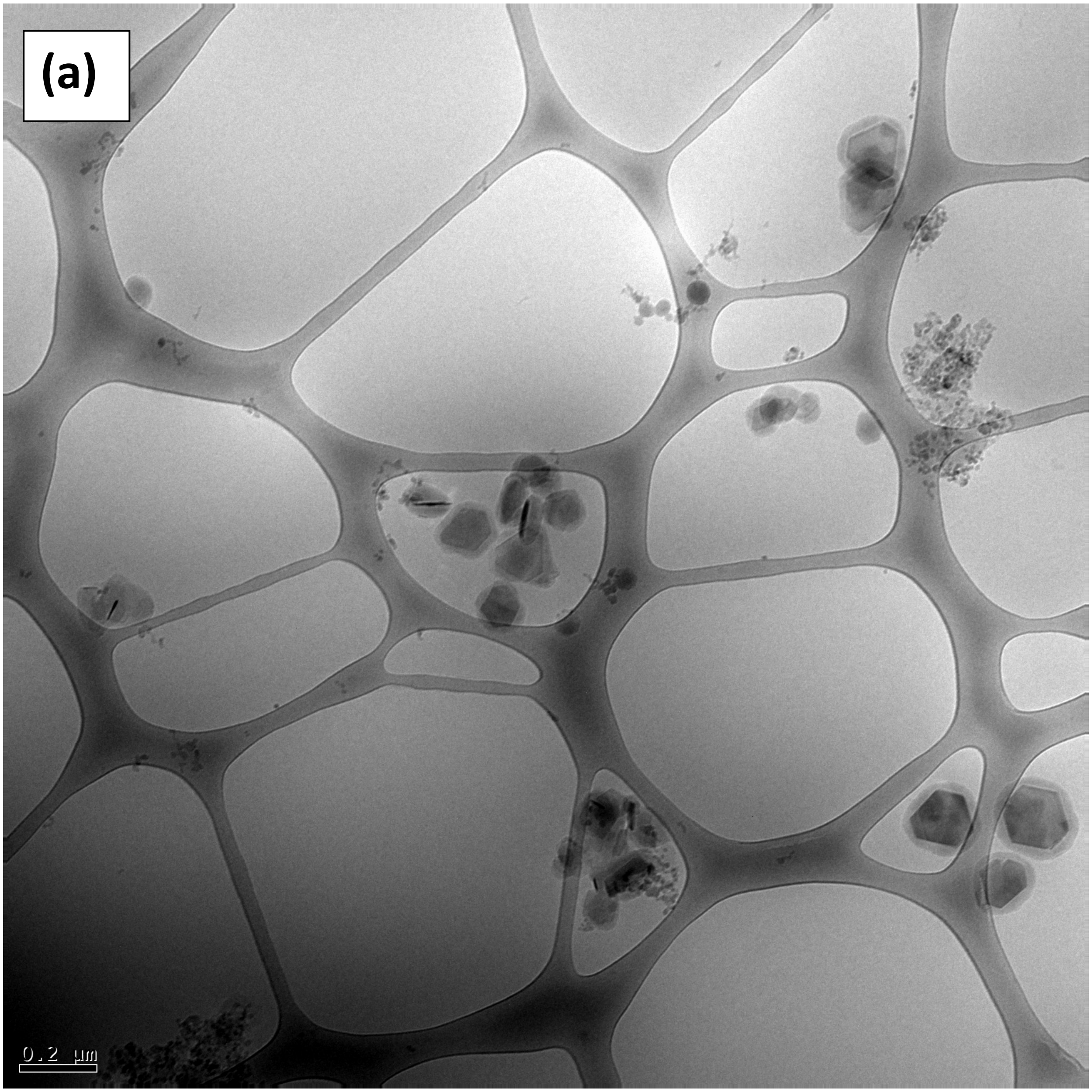
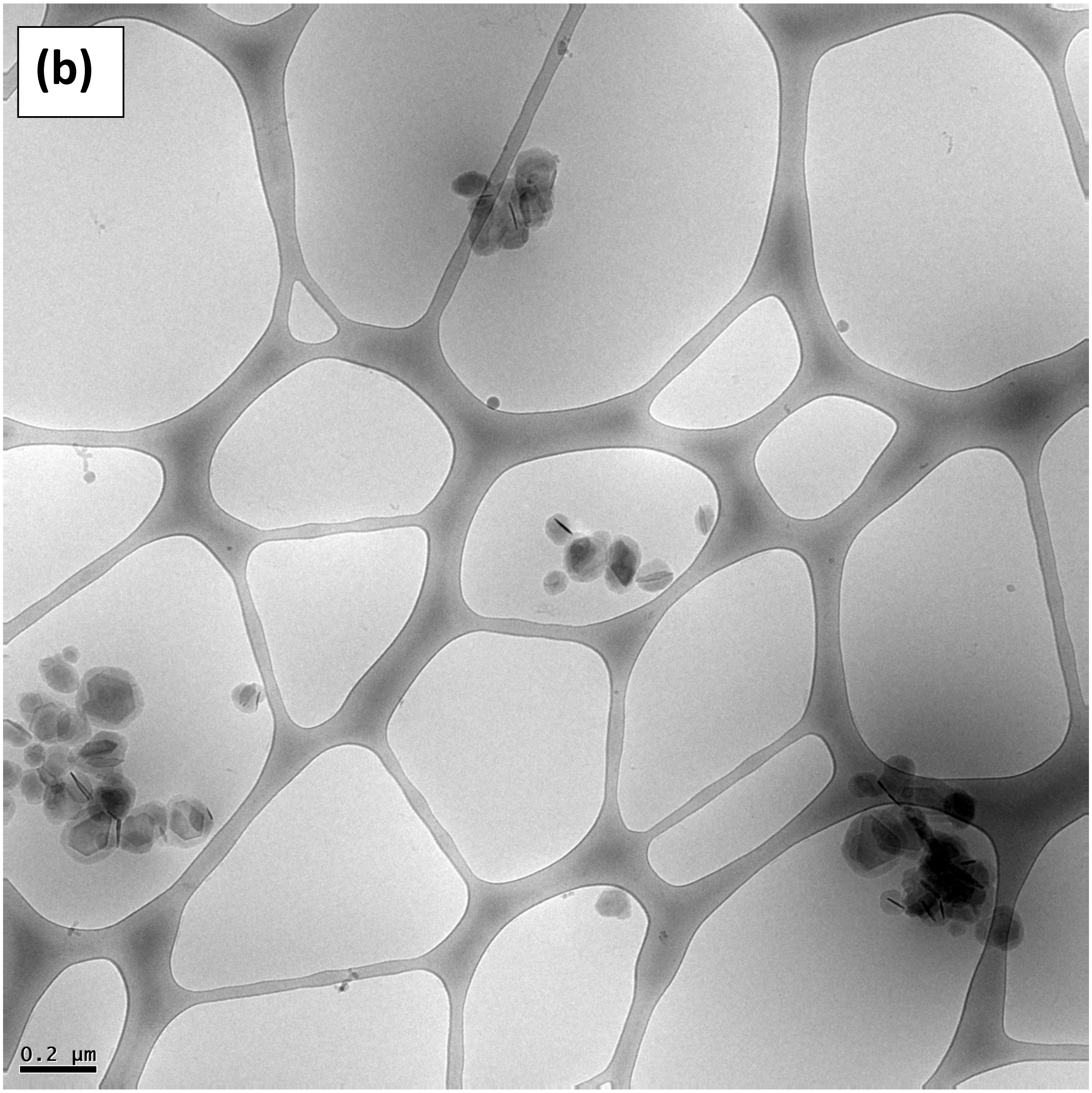


Fig. S3 Diameter distribution curves by number (a), volumes (b), and intensity (c) of polymer-Gibbsite latex particles obtained using profile *II*. Other conditions as in Fig. S1.

The following (cryo-)TEM images were used for particle counting: profile II (Fig. S4) and III (Fig. S5).




(b)
0.2 µm

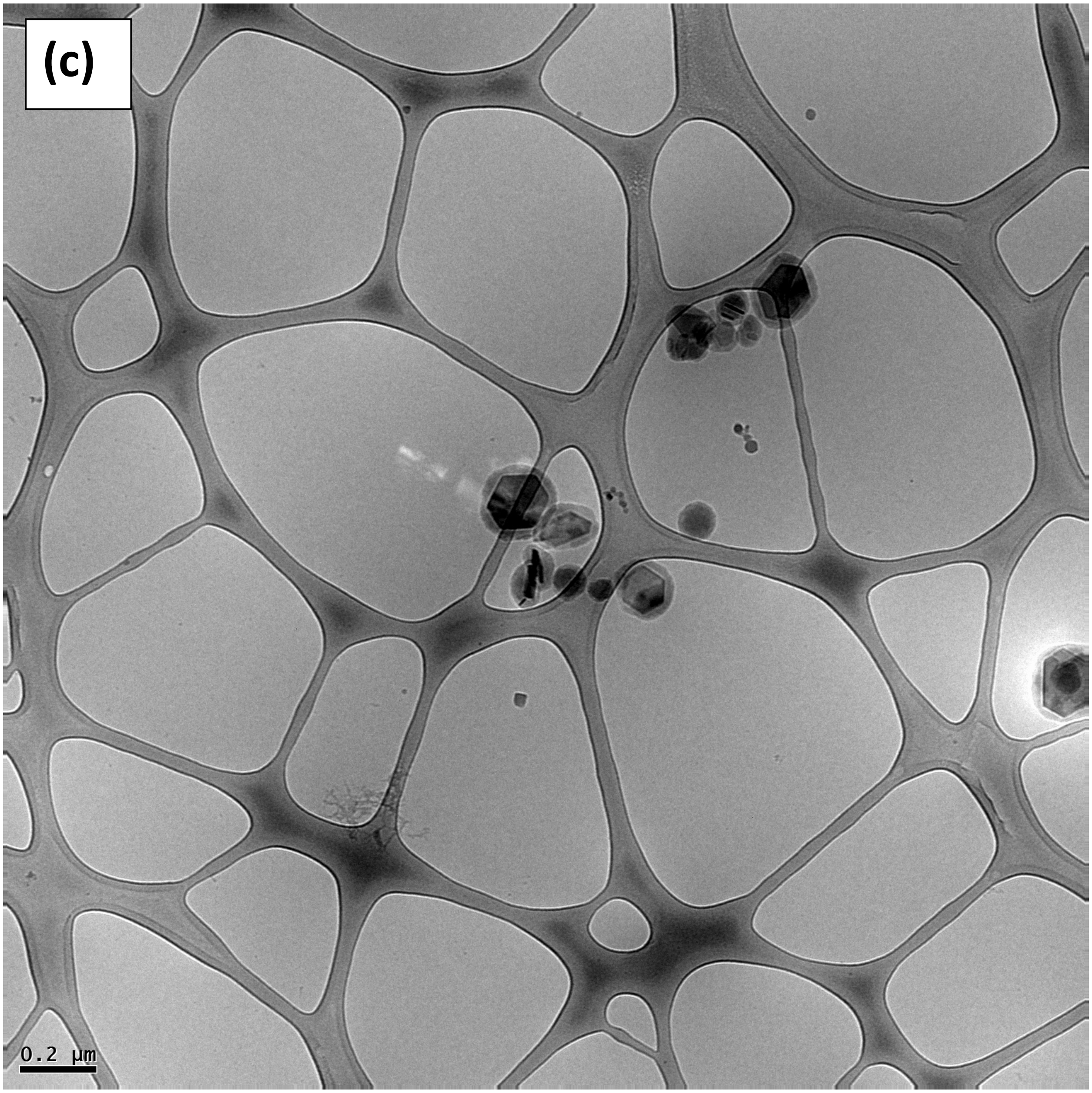
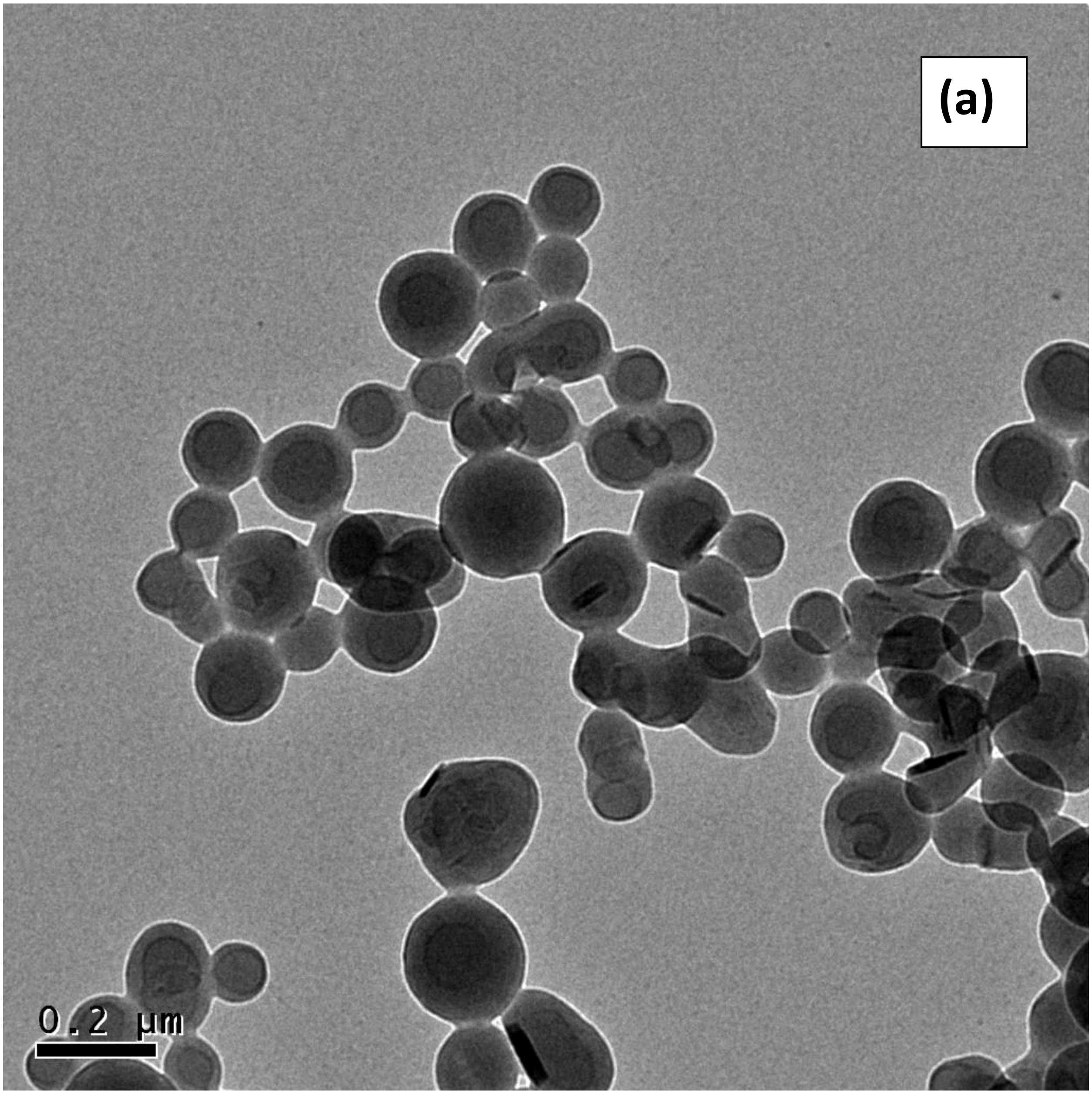
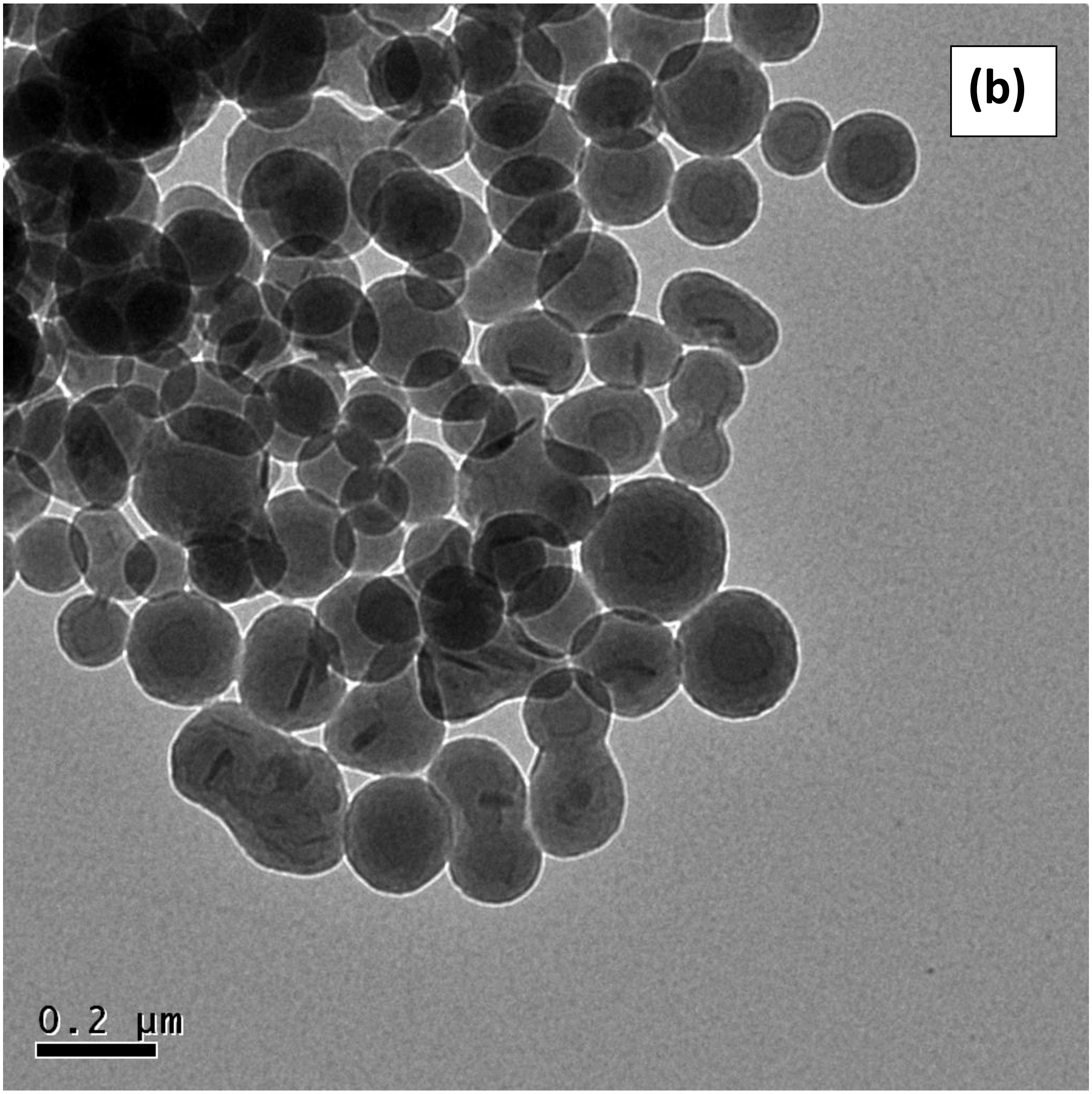


Fig. S4 (a-c) cryo-TEM images of polymer-Gibbsite latex particles obtained using profile II at EGDMA content of 10 wt%.


(a)
0.2 µm


(b)
0.2 µm

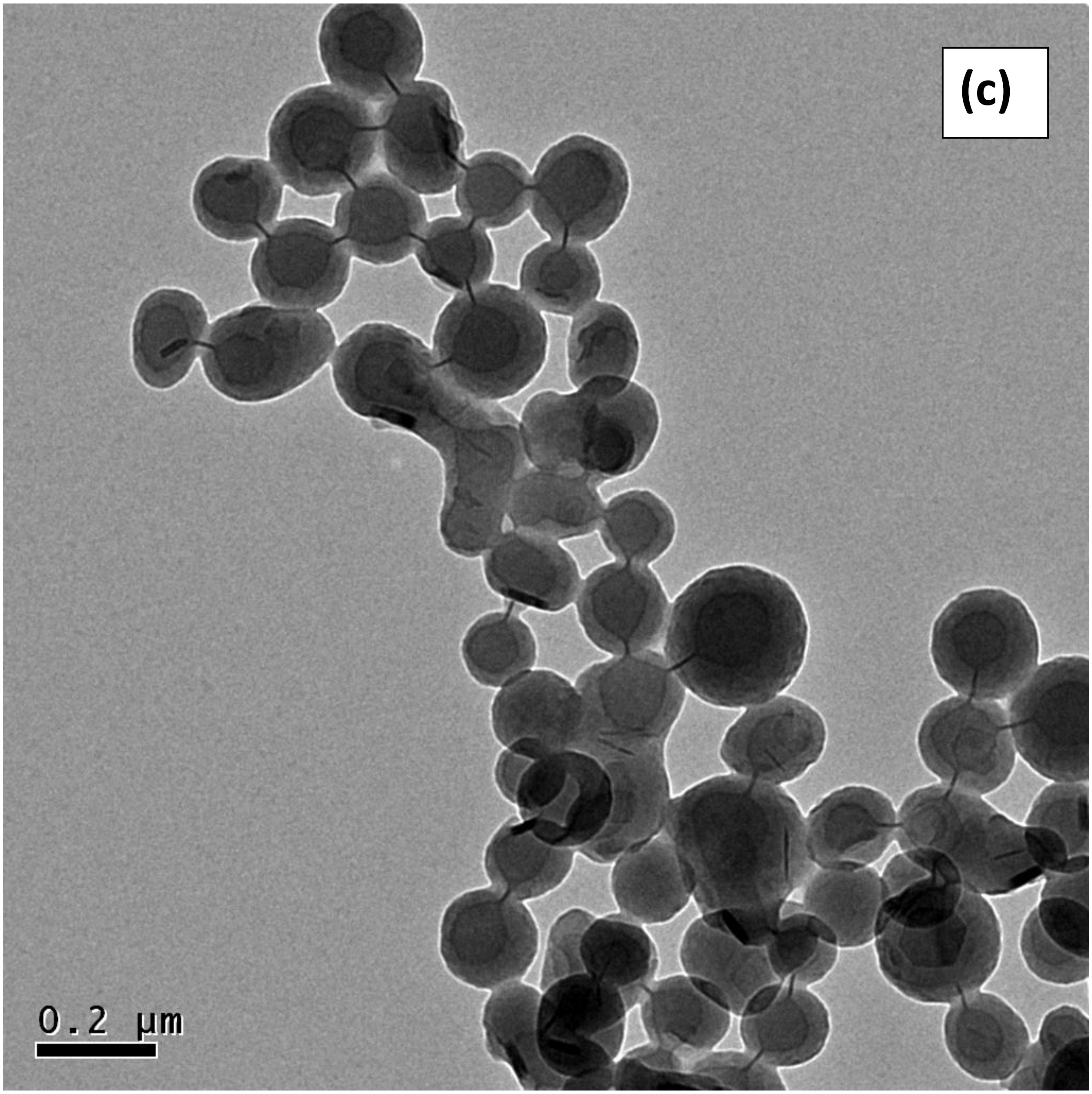


Fig. S5 (a-c) TEM images of polymer-Gibbsite latex particles obtained using profile *III* at EGDMA content of 10 wt%.

Effect of EGDMA concentration

Evolution of the *Z*-average diameter and the zeta-potential during the reaction at different EGDMA content is presented on Fig. S6.

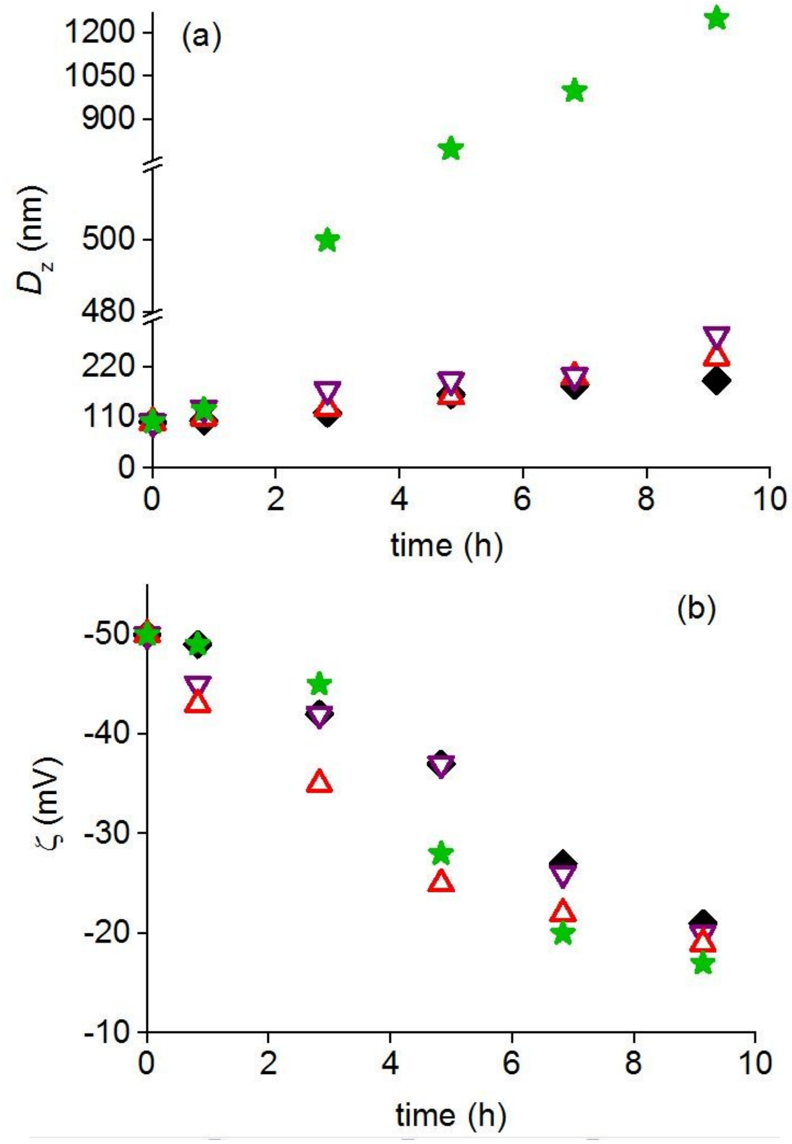


Fig. S6 Evolution of the Z-average particle diameter D_z (a) and the ζ-potential (b) obtained using profile *II* at different EGDMA contents: (🕘) 5 wt%, (♦) 10 wt%, (❐) 15 wt% and (★) 20 wt%. Other conditions as in Fig. S1.

References

[1] A. M. Wierenga, T. A. J. Lenstra and A. P. Philipse, *Colloids Surf.*, 1998, **134**, 359-371.

[2] O. P. Loiko, A. B. Spoelstra, A. M. van Herk, J. Meuldijk and J.P.A. Heuts, *Polym. Chem.*, 2016, **7**, 3383-3391.