

Electronic Supplementary Information (ESI)

**Ambient temperature synthesis of narrow or monodisperse, highly cross-linked,
and “living” polymer microspheres by atom transfer radical precipitation
polymerization**

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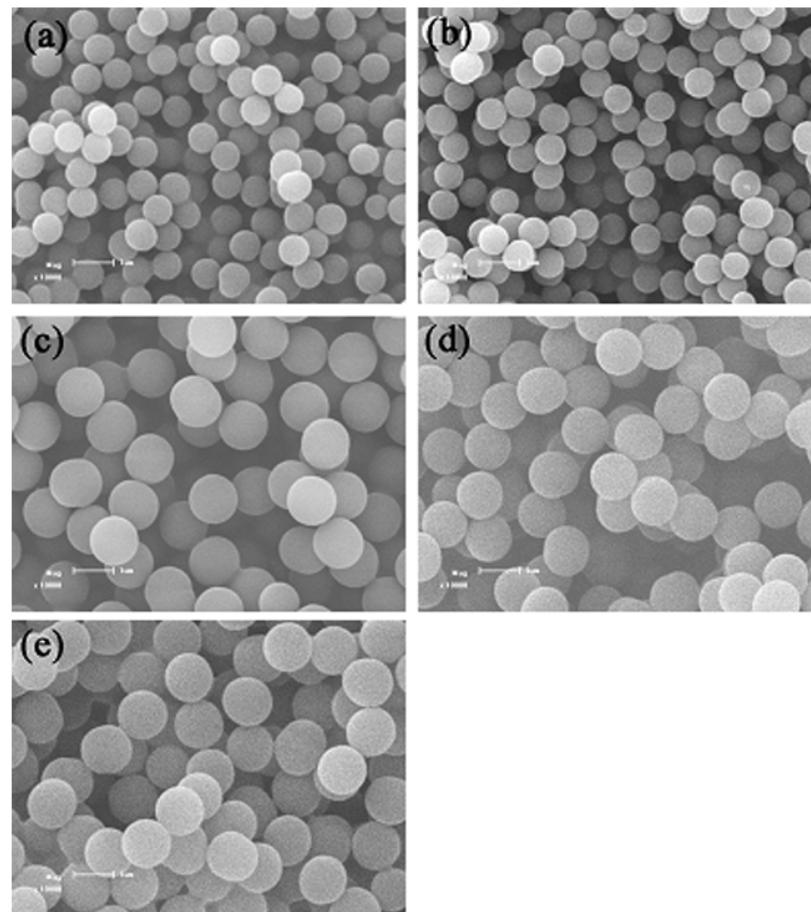


Fig. S1 SEM images of two series of repetition batches of poly(4-VP-*co*-EGDMA) microspheres prepared by ambient temperature ATRPP in 2-propanol with a monomer loading of 1.0 vol% (a, b) and 2.0 vol% (c, d, and e), respectively (the samples a, b, c, d, and e correspond to entries 2a, 2b, 5a, 5b, and 5c in Table 1, respectively). The scale bar corresponds to 1 μm in parts a-e.

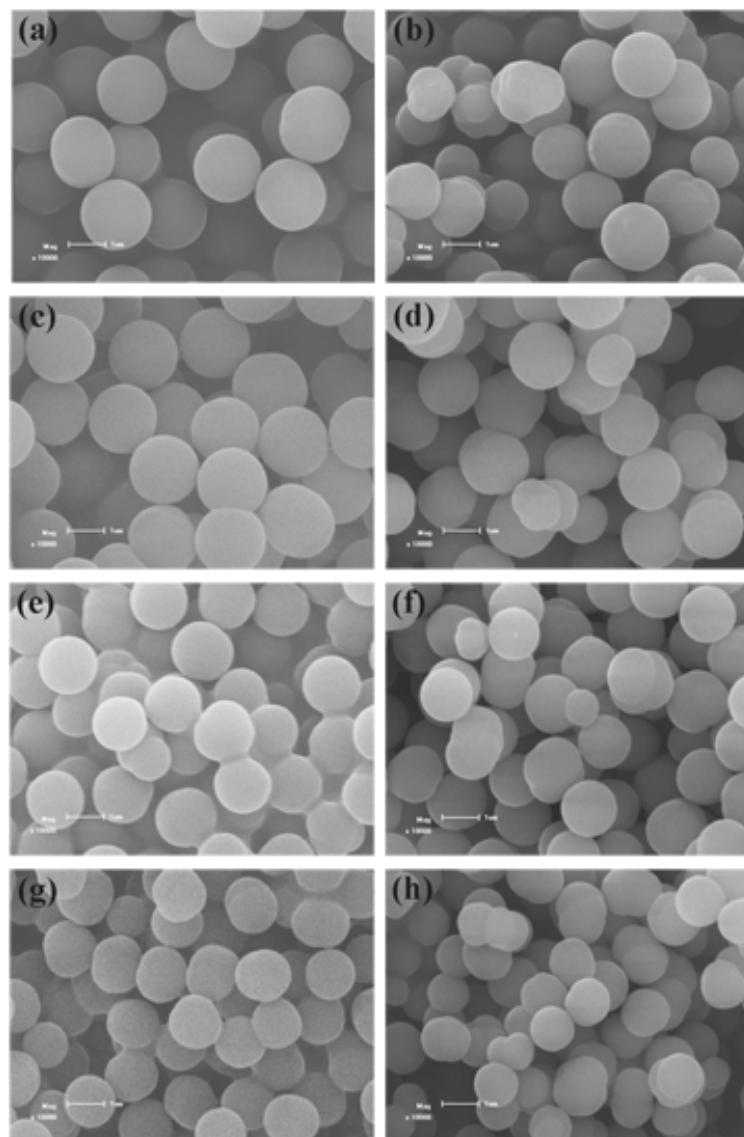


Fig. S2 SEM images of poly(4-VP-*co*-EGDMA) microspheres prepared by ambient temperature ATRPP for 24 h in 2-propanol (a,b), 1-propanol (c,d), 1-butanol (e,f), and 1-pentanol (g,h), respectively (The monomer loading in 2-propanol was 3.0 vol% and those in other alcohols were 2.0 vol%. The samples a, c, e, and g correspond to entries 6, 26, 30, and 34 in Table 1, respectively, and they were obtained from the suspension solutions after the polymerization; The sample b, d, f, and h also correspond to entries 6, 26, 30, and 34 in Table 1, respectively, but they represented the polymer particles precipitated onto the bottom of the reaction flasks during the polymerization processes). The scale bar corresponds to 1 μm in all the figures.

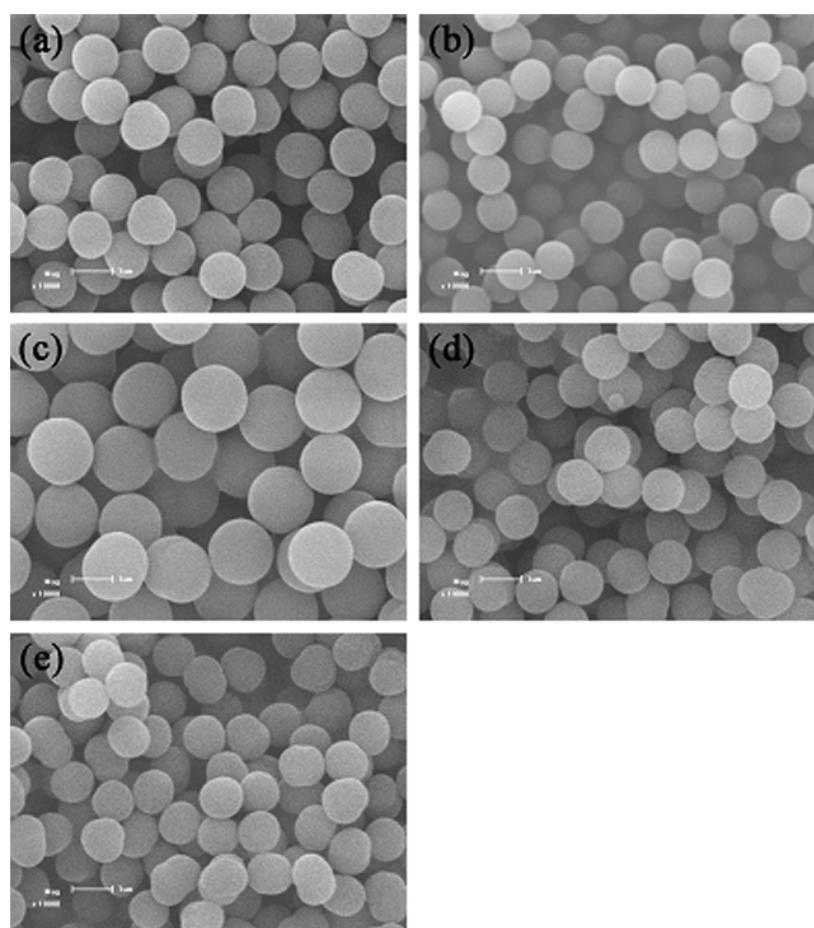


Fig. S3 SEM images of poly(4-VP-*co*-EGDMA) microspheres prepared by ambient temperature ATRPP at a polymerization time of 7 h in 2-propanol (a), methanol (b), 1-propanol (c), 1-butanol (d), and 1-pentanol (e), respectively (the monomer loading in 2-propanol was 3.0 vol% and those in other alcohols were 2.0 vol%) (the samples a, b, c, d, and e correspond to entries 7, 19, 27, 31, and 35 in Table 1, respectively). The scale bar corresponds to 1 μm in parts a-e.

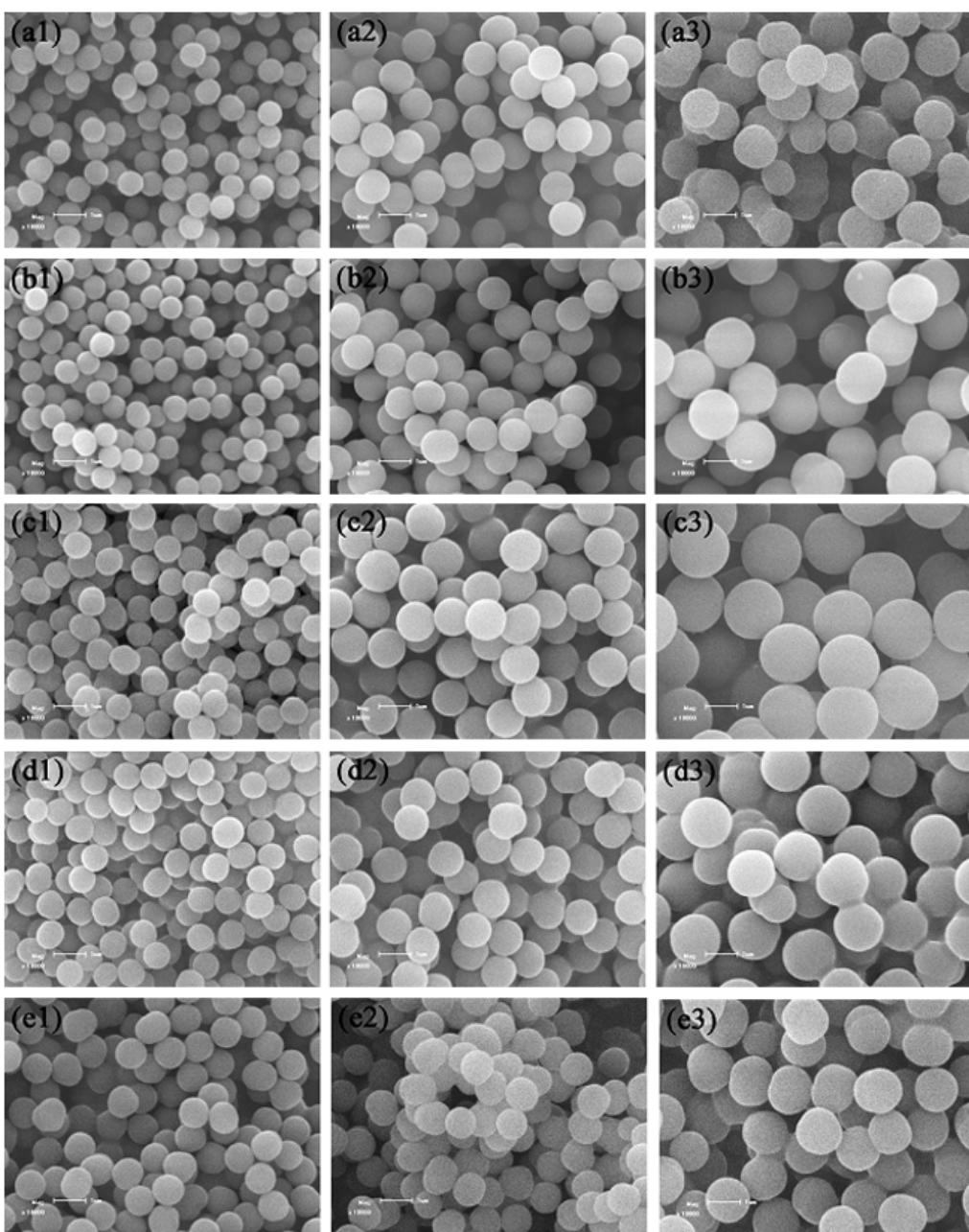


Fig. S4 SEM images of poly(4-VP-*co*-EGDMA) microspheres prepared by ambient temperature ATRPP for 24 h in methanol (a1-a3), ethanol (b1-b3), 1-propanol (c1-c3), 1-butanol (d1-d3), and 1-pentanol (e1-e3), respectively (monomer loading = 0.8 vol% (a1,b1,c1,d1,e1), 1.4 vol% (a2,b2,c2,d2,e2), and 2.0 vol% (a3,b3,c3,d3,e3)) (the samples a1-a3, b1-b3, c1-c3, d1-d3, and e1-e3 correspond to entries 16-18, 20-22, 24-26, 28-30, and 32-34 in Table 1, respectively; all the samples were obtained from the suspension solutions after the polymerization except that the sample a3 represented the polymer particles precipitated onto the bottom of the reaction flask during the polymerization process). The scale bar corresponds to 1 μ m in all the figures.

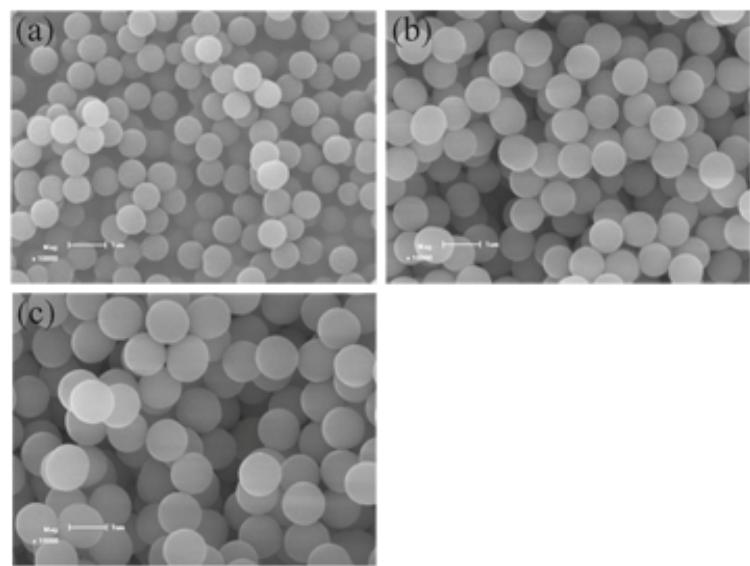


Fig. S5 SEM images of poly(4-VP-*co*-EGDMA) microspheres prepared by ATRPP in 2-propanol for 24 h at 25 (a), 40 (b), and 60 °C (c), respectively (The sample a corresponds to entry 2a in Table 1, and samples b and c were prepared under the same conditions with sample a except that the reaction temperatures were different). The scale bar corresponds to 1 μm in parts a-c.

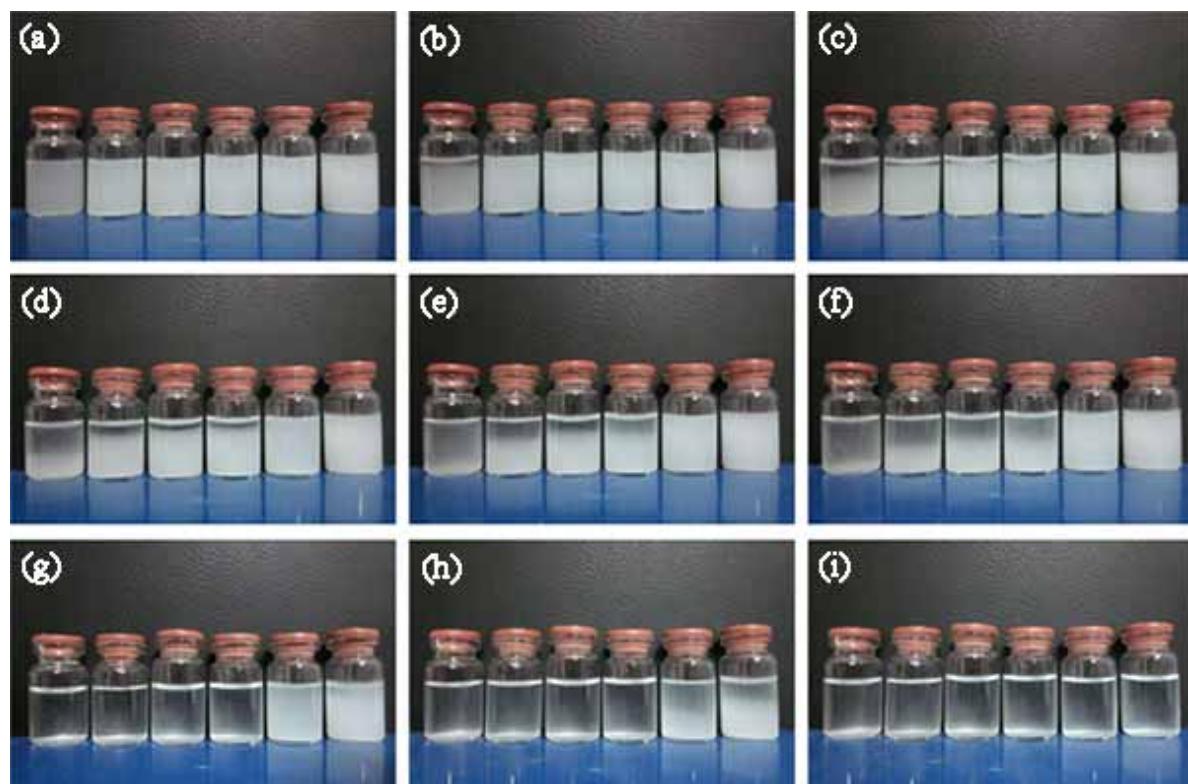


Fig. S6 The detailed photographs for the dispersion stability of polymer microspheres in water (1 mg/mL) at 25 °C after their ultrasonically dispersed solutions being settled down for 0 (a), 0.5 (b), 1 (c), 1.5 (d), 2 (e), 3 (f), 5 (g), 8 (h), and 12 h (i), respectively. The samples located from left to right in each photograph are poly(4-VP-*co*-EGDMA), poly(GMA-*co*-EGDMA), poly(MMA-*co*-EGDMA), poly(HEMA-*co*-EGDMA), PHEMA brushes-grafted poly(4-VP-*co*-EGDMA), and PNIPAAm brushes-grafted poly(4-VP-*co*-EGDMA) microspheres, respectively.