Supporting Information for:

Functionalization of liquid metal nanoparticles via RAFT process

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Additional Figures



Figure S1. ¹H NMR spectrum of the CDPA-ester (DMSO-*d*₆, 400 MHz).



Figure S2. ¹³C NMR spectrum of CDPA-ester (CDCl₃, 150 MHz).



Figure S3. High resolution MS for CDPA-ester ($[M + H]^+ C_{20}H_{36}NO_2S_3$, 418.1908; found, 418.1909).



Figure S4. ¹H NMR spectrum of the xanthate (CDCl₃, 400 MHz).



Figure S5. The ¹H NMR spectra comparison of pure CDPA before and after 4 hours sonication in THF. *No clear changes were observed, which indicates that the CDPA is stable under the experimental sonication condition.*



Figure S6. The ¹H NMR spectra comparison of CTPA before and after 4 hours sonication in THF. *The CTPA is generally stable, however, a small degree of decomposition was observed as some new peaks were found at 1.0-2.0 ppm and 6.5-7.0 ppm.*



Figure S7. The ¹H NMR spectra comparison of Xanthate before and after 4 hours sonication in THF. *No clear changes were observed, which indicates that the Xanthate is stable under the experimental sonication condition.*



Figure S8. TEM images of EGaIn nanoparticles prepared in the presence of different amount of CDPA. (100 mg EGaIn, 1.5 mL THF, 4 hours sonication)



Figure S9. XPS spectra of EGaIn@CDPA, a) Ga 3d spectrum and b) In 3d spectrum.



Figure S10. The effect of the RAFT agents on stability and morphology of EGaIn nanoparticle. The RAFT agents and corresponding EGaIn nanoparticle suspensions at different time, and corresponding TEM images of EGaIn nanoparticles; a-a4) BTPA, b-b4) Xanthate, c-c4) CTPA.



Figure S11. Dependence of M_n and \overline{D} on the monomer conversion of CDPA controlled polymerization of MMA with EGaIn nanoparticles.

Method for determining the amount of free polymers.

Another batch of EGaIn@PMMA was synthesized in the same procedure as described in the Experimental section. The monomer conversion (~67.3%, theoretical molecular weight =13,860 g/mol) was determined via ¹H NMR spectroscopy by dissolving crude solution in CDCl₃. 2 mL of the reaction was diluted with 4 mL of THF. Another 2 mL of the resulting suspension was transferred to a centrifuge tube and centrifuged at 4000 rpm for 10 minutes to allow the majority of the particles to settle down at the bottom of the tube. The up-layer liquid was transferred to a vial, and one drop of concentrated HCl was added to remove any residual EGaIn particles. The solvent was transferred to a weighed vial and dried completely under vacuum to determine the amount of free polymers (A=135.2 mg). Meanwhile, 2 mL of THF was added to the settled EGaIn particles inside the centrifuge tube, and several drops of concentrated HCl was then added to the redispersed particles to allow the separation of polymers from the surface of EGaIn particles. The clear liquid was then transferred to a weighed vial and dried completely under vacuum to determine the amount of grafted polymers (B=78.0 mg). The molecular weights of both free polymers and attached polymers were determined by DMF SEC.

The percentage of grafted polymers = $B/(A+B) \times 100\% = 36.6\%$.

The percentage of free polymers = $A/(A+B) \times 100\% = 63.4\%$.



Figure S12. SEC curves of free PMMA and grafted PMMA separated by centrifuge. Free PMMA, $M_n = 16,000 \text{ g/mol}$, D = 1.16, grafted PMMA, $M_n = 15,500 \text{ g/mol}$, D = 1.19. (DMF as eluent, PMMA standards)



Figure S13. ¹H NMR spectrum of the EGaIn@PMMA₁₀₆, (CDCl₃, 400 MHz).



Figure S14. SEC curve of the PMMA₁₀₆ detached from EGaIn@PMMA₁₀₆, M_n =13,200 g/mol, D= 1.16. (DMF as eluent, PMMA standards)



Figure S15. ¹H NMR spectrum of the EGaIn@PBA₃₈₃, (CDCl₃, 400 MHz).



Figure S16. SEC curve of the PBA₃₈₃ detached from EGaIn@PBA₃₈₃, $M_n = 22,200 \text{ g/mol}$, D = 1.35. (DMF as eluent, PS standards)



Figure S17. ¹H NMR spectrum of the EGaIn@PDMA₁₉₈, (CDCl₃, 400 MHz).



Figure S18. SEC curve of the PDMA₁₉₈ detached from EGaIn@PDMA₁₉₈, M_n =22,000 g/mol, D= 1.27. (DMF as eluent, PMMA standards)



Figure S19. ¹H NMR spectrum of the EGaIn@PS₂₅₅, (CDCl₃, 400 MHz).



Figure S20. SEC curve of the PS₂₅₅ detached from EGaIn@PS₂₅₅, M_n =26,700 g/mol, D= 1.12. (DMF as eluent, PS standards)



Figure S21. ¹H NMR spectrum of the EGaIn@POEGMA₂₃, (CDCl₃, 400 MHz).



Figure S22. SEC curve of the POEGMA₂₃ detached from EGaIn@POEGMA₂₃, M_n =15,000 g/mol, D= 1.19. (DMF as eluent, PMMA standards)



Figure S23. TGA curves comparison of EGaIn and EGaIn coated with different types of polymers. All samples were analyzed under N_2 atmosphere, therefore, the pure EGaIn sample did not show any mass loss or gain in the analysis temperature range. The residual mass at around 500 °C was assigned to EGaIn; EGaIn@PMMA contains 30.0% EGaIn, EGaIn @PBA contains 13.3% EGaIn, the mass decreasing for EGaIn @PDMA before 150 °C might result from the instability of balance, therefore, the corrected EGaIn percentage is 16.2%.



Figure S24. The dispersion tests of EGaIn@PDMA in different solvents.



Figure S25. ¹H NMR spectrum of the EGaIn@PMMA₁₀₆-*b*-POEGMA₂₀, (CDCl₃, 400 MHz).



Figure S26. ¹H NMR spectrum of the EGaIn@PMMA₁₀₆-*b*-PDMA₁₁₇, (CDCl₃, 400 MHz).



Figure S27. SEC curve of the PMMA₁₀₆-*b*-PDMA₁₁₇ detached from EGaIn@PMMA₁₀₆-*b*-PDMA₁₁₇, M_n =23,300 g/mol, D= 1.28. (DMF as eluent, PMMA standards)