

Supporting Information

Hydrophilization of Magnetic Nanoparticles with Modified Alternating Copolymers. Part 1: The influence of the grafting

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1. TEM image of iron oxide nanoparticles

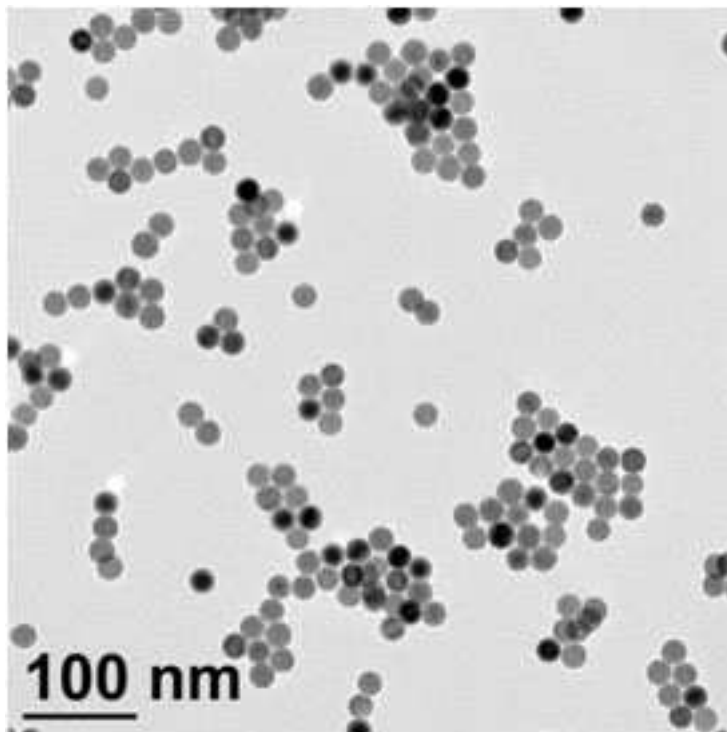


Figure S1. TEM image of 21.6 nm NPs.

2. Synthesis of modified PMAcOD samples

Table S1. The amounts of reagents for the modified PMAOD synthesis.

Sample notation	PMAOD:PEG (EG) mole ratio	PMAOD:PEG-NH ₂ (5,000) (P series), mg	PMAOD:PEG-NH ₂ (S series), mg	PMAOD:EG (G series), mg	Yields, %
1 (P1, S1, G1)	1:20	15:37.5	25:9.37	50:2.25	98, 97, 98
2 (P2, S2, G2)	1:30	10:37.5	25:14.05	50:3.4	97, 96, 98
3 (P3, S3, G3)	1:60	7.5:56	25:28.13	50:6.8	96, 87, 97
4 (P4)	1:80	5:50	-	-	98

3. NMR studies of the degree of grafting

NMR studies were employed to identify the proportion of grafting at different conditions. First PMAOD, PEG-NH₂ with MW750 and MW5000 were prepared in CDCl₃ for spectral assignments. A series of modified PMAOD, namely S2, S3, P3, P4, and G3 were prepared for quantitative measurements.

The PEG-NH₂ ¹³C spectra (Fig. S2a) showed that all carbons had very sharp peaks, as expected for small molecules. ¹³C chemical shifts were determined to be 41.7ppm for NH₂*CH₂CH₂O, 73.3ppm for NH₂CH₂*CH₂O, 71.8ppm for *CH₂OCH₃, 58.9ppm for CH₂O*CH₃, and 70.5ppm and 70.2ppm for the rest of carbons, respectively. The PMAOD ¹³C spectra (Fig. S2b) showed very sharp peaks for the flexible alkyl chains and very broad peaks for the rigid backbone of this polymer. Those broad peaks were only visible when a very large number of scans was performed and a large line-broadening factor was used for data processing to reduce noise. ¹³C chemical shifts of the sharp peaks were 14.1ppm for CH₂CH₂CH₂*CH₃, 22.7ppm for CH₂CH₂*CH₂CH₃, 31.9ppm for CH₂*CH₂CH₂CH₃, 29.4ppm for *CH₂CH₂CH₂CH₃, and 29.8ppm for the other flexible carbons, respectively. In the spectra of the copolymers (as shown in Fig. S2c for S2), the NH₂*CH₂CH₂O (41.7ppm) peak and the NH₂CH₂*CH₂O peak (73.3ppm) observed in the PEG-NH₂ ¹³C spectra disappear while all the other sharp peaks observed in the above PEG-NH₂ and PMAOD spectra were still well visible with no noticeable change

of their chemical shift or peak width.. This indicates that PMAOD and PEG-NH₂ formed PMAOD-NH-PEG copolymer with the NH end of PEG-NH₂ connected to the backbone of PMAOD.

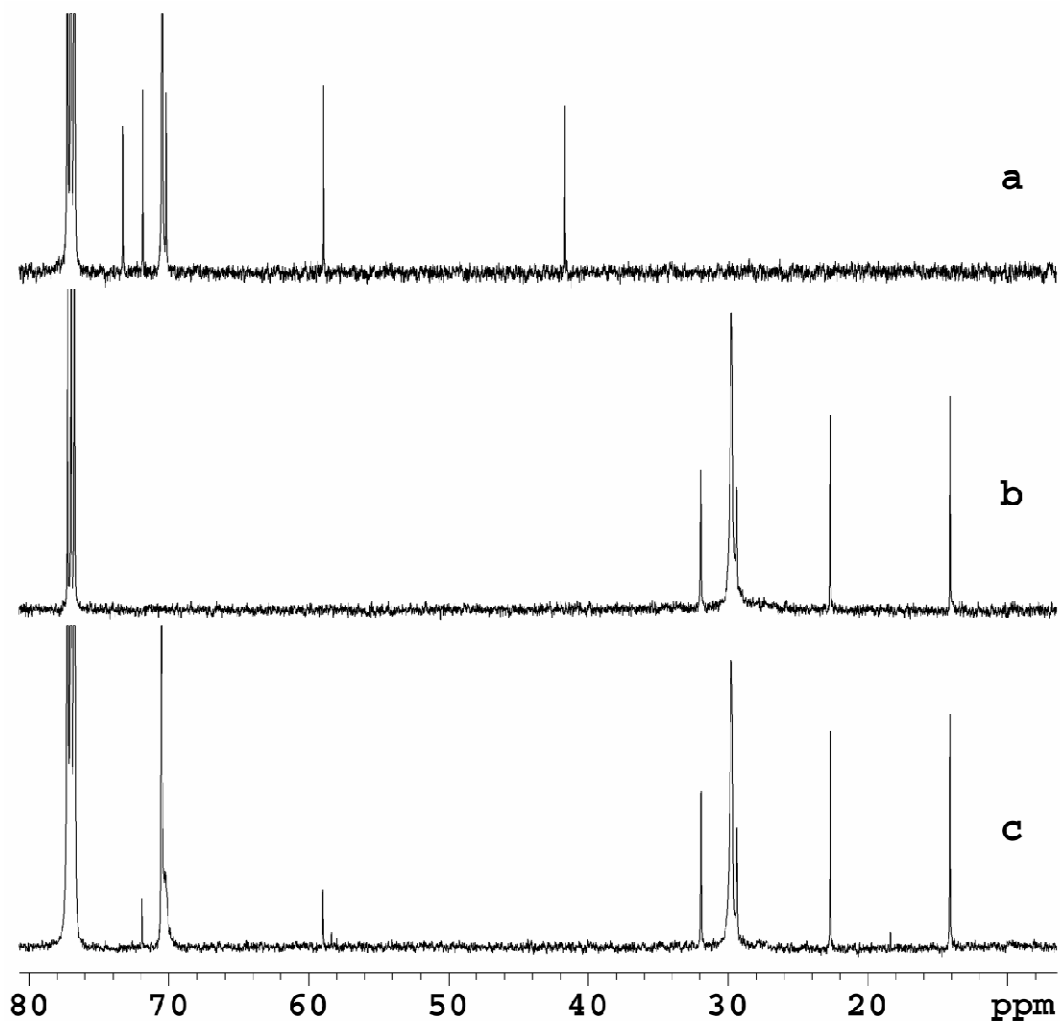


Figure S2. The inverse gated decoupling ¹³C spectra of PEG-NH₂ (a), PMAOD (b), and S2 (c) in CDCl₃ at 25°C. No residual NH₂*CH₂CH₂O peak (41.7ppm) or residual NH₂CH₂*CH₂O peak (73.3ppm) was detected, indicating a complete reaction of PEG-NH₂ with PMAOD.

The PEG/PMAOD ratios of the P, S, and G copolymers were determined by quantitative ¹³C NMR measurements. The integral intensities for all (sharp) peaks on the modified PMAOD spectra were measured. Average integral intensities of two peaks (71.8 and 58.9ppm) for PEG-NH and of three peaks (31.9, 22.7, and 14.1ppm) for PMAOD were used to calculate the PEG/PMAOD ratio. For the solutions

with concentration of 6.3×10^{-4} mole, the PEG/PMAOD ratios determined by NMR for each copolymer were in agreement with Table I within $\pm 10\%$. The unreacted PEG-NH₂ could be detected from appearance of a residual NH₂*CH₂CH₂O peak at 41.7ppm (or/and a residual NH₂CH₂*CH₂O peak at 73.3ppm). For all the copolymer samples (with the concentration of 6.3×10^{-4} mole) measured in this study no residual NH₂*CH₂CH₂O peak was detected, with the exception of S3 copolymer. The disappearance of the NH₂*CH₂CH₂O peak indicates a complete reaction of PEG-NH₂ with PMAOD. For the S3 sample two residual peaks of NH₂*CH₂*CH₂O were observed with medium peak width. The existence of the two residual peaks indicates an incomplete reaction of PEG-NH₂ with PMAOD. Unreacted fraction was determined to be about 20%. The medium peak width might be due to the interaction of the amine group of unreacted PEG-NH₂ with some groups of the copolymer, impeding mobility. When this copolymer was measured at 80°C in CD₂ClCD₂Cl, the two residual peaks turned into sharp peaks. This might imply that some hydrogen bonds were formed between PEG-NH₂ and PMAOD at room temperature. When the synthesis of modified PMAOD was carried out at the 1/5 concentration than those presented in Table 1, the P1, P2, G1, G2 samples showed the complete attachment, while for P3, only about 30% tails were attached, revealing a need to carry out these reactions at higher concentrations.

4. TGA data

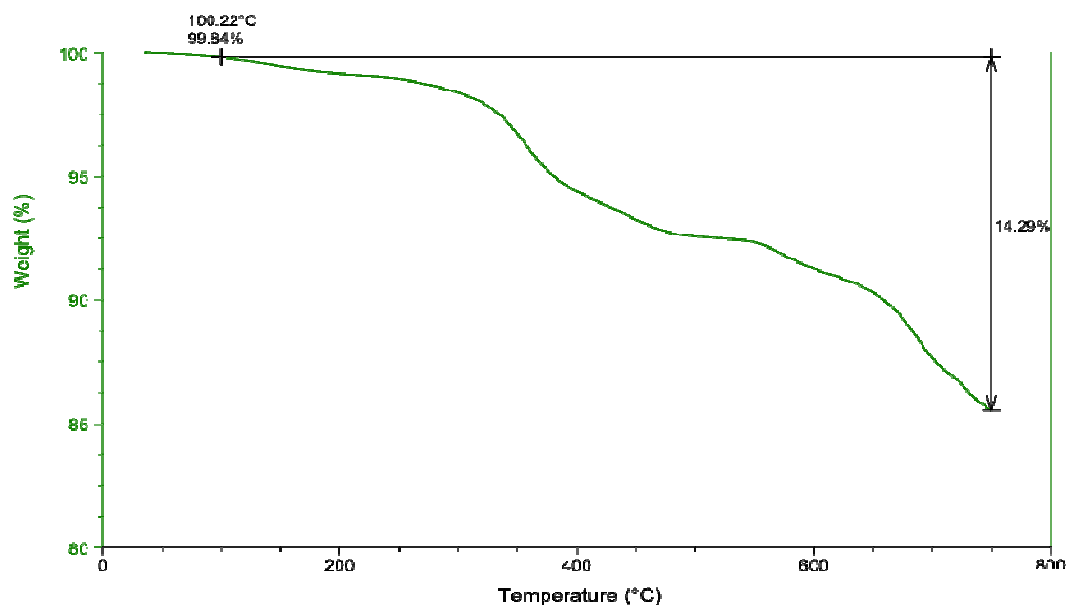


Figure S3. Weight loss as a function of temperature for NPs coated with oleic acid.

Figure S4 shows a typical TGA curve for G1 coated NPs.

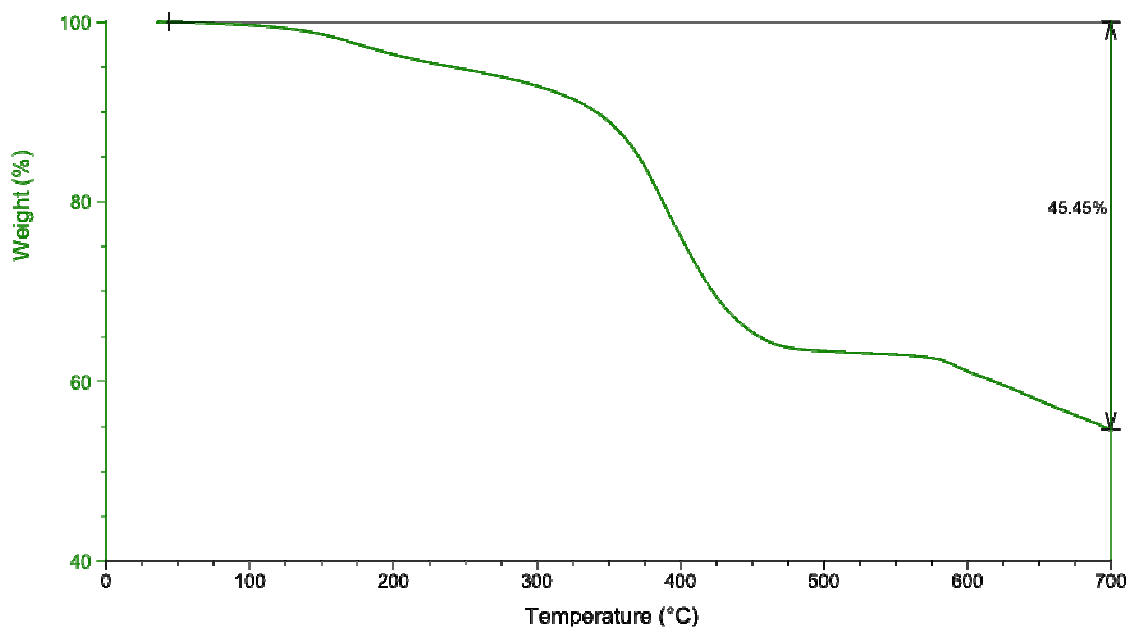


Figure S4. Weight loss as a function of temperature for G1 coated NPs.

Total mass lost from 100 °C to 700 °C was determined to avoid any additional loss from water. The amount of oleic acid that makes up the shell, as previously determined by TGA experiments on uncoated NP, was subtracted from the total to find out the weight of modified PMAOD that was lost. This weight was divided by the combined molecular weight of the polymer and multiplied by Avogadro's number to calculate the number of modified PMAOD molecules lost. This was further divided by a number of nanoparticles that were in the pan to calculate the number of coat molecules per nanoparticle. To calculate the amount of nanoparticles that were used in the TGA experiments, final mass, that was assumed to be purely iron oxide nanoparticles, was divided by a mass of a single NP, as calculated from the volume and the density (5.7 g/cm^3 for FeO, the major phase of reported NPs).