Supplementary information:

Water-Soluble Dendritic-linear Triblock Copolymers-Modified Magnetic Nanoparticles: Preparation, Characterization and Drug Release Properties.

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1. Experimental section

1.1 Synthesis of 2-Azidoethanol

2-Chloroethanol (6.0 g, 75 mmol), sodium azide (9.7 g, 150 mmol), tetrabutylammonium iodide (3.0 g, 8 mmol) and 2-butanone(40 mL) were added into a 250 mL three-neck round-bottom flask equipped with a condenser, and the reaction mixture was stirred with a magnetic bar under nitrogen protection at 80 ^{o}C for 24 h. After the undissolved solid was removed by filtration, a yellow oil residue can be obtained by removal the solvent 2-butanone on a rotary evaporator. The obtained yellow oil residue was distilled under reduced pressure to give a colorless oil product (yield: 4.8 g, 74%). ^{1}H NMR (500MHz, $CDCl_3$), δ (TMS, *ppm*): 4.79 (2H, C**H**$_2$OH), 1.97 (1H, C**H**$_2$OH), 3.48 (2H, C**H**$_2$N$_3$).

1.2 Synthesis of 2'-azidoethyl 2-bromoisobutylate (AEBIB)

2-Azidoethanol (2.0 g, 23 mmol), anhydrous Et_3N (3.9 mL, 27.8 mmol) and dry methylene chloride (30 mL) were added into a 150 mL two-neck round-bottom flask equipped with a 20 mL dropping funnel. The funnel was charged with 2-bromoisobutyryl bromide (5.8 g, 25 mmol) and dry methylene chloride (15 mL). The flask was immersed into an ice-water bath and the mixture was stirred with a magnetic bar under nitrogen atmosphere. Then, the 2-bromoisobutyryl bromide solution was added dropwise into the flask over a period of 1 h. After the addition was completed, the reaction mixture was continually stirred at 0 ^{o}C for 2 h and then at room temperature for another 16 h. After removal of the undissolved solid, the solution

was washed successively with distilled water (3 × 70 mL). The organic phase was then dried over anhydrous $MgSO_4$ overnight. After filtration, methylene chloride was removed by rotary evaporation, and the residue was further purified by a silica gel column chromatograph using CH_2Cl_2/petroleum ether (1:1 v/v) as an eluent. The solvents was removed by rotary evaporation and AEBIB as a colorless oil was obtained (4.9 g, yield: 91%). ^{1}H NMR (500MHz, $CDCl_3$), δ (TMS, *ppm*): 4.34 (2H, -COOC**H**$_2$CH$_2$N$_3$), 3.52 (2H, -COOCH$_2$C**H**$_2$N$_3$), and 1.96 (6H, -C(C**H**$_3$)$_2$Br)

1.3 Synthesis of propargyl focal point PAMAM-typed dendron (Propargyl-$D_{2.0}$-COOH)

The propargyl focal point PAMAM-typed dendron with primary amine groups ($D_{1.0}$ and $D_{2.0}$) was synthesized using a similar method reported by Dong et al. [1]

In a 100 ml round-bottom flask, 2 g of $D_{2.0}$ was dissolved in the mixture solvent of 15 ml DMF and 15 ml methanol. 3.3 g of succinic anhydride was then added into the mixture solution at 0 °C. The mixture was stirred vigorously for 1 h at 0 °C and then for another 24 h at room temperature. The reaction solution was concentrated by rotary evaporation, and 10ml of water was then added. After stirring for 30 min, the solution was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic phase was dried over anhydrous $MgSO_4$ overnight. After filtration, the filtrate was evaporated on a rotary evaporator to give a colorless liquid product (2.46 g, 85%). ^{1}H NMR (500MHz, D_2O), δ (TMS, *ppm*): 2.28 (1H, -C**H**CCH$_2$-), 2.33(28H, -C**H**$_2$CONH-), 2.56(4H, -C**H**$_2$NR$_2$-), 2.74(12H, RNC**H**$_2$-), 3.18(16H, -HNCH$_2$CH$_2$NH-), 3.23(4H, -HNC**H**$_2$-), 3.30(2H, -CHCC**H**$_2$-).

1.4 Procedure for obtaining functional copolymers from the modified magnetic nanoparticles

The functional copolymers, $D_{2.0}$-*b*-PDMAEMA-Br and $D_{2.0}$-*b*-PDMAEMA-*b*-PNIPAM, were obtained by immersing the Fe_3O_4-$D_{2.0}$-*b*-PDMAEMA-Br and Fe_3O_4-$D_{2.0}$-*b*-PDMAEMA-*b*-PNIPAM nanoparticles in a 14% aqueous solution of HCl at room temperature for 1 h, respectively. The resulting products were purified by dialyzing against deionized water until the pH value of the solution approached pH 7. The functional copolymers were obtained by lyophilization and characterized by GPC and ^{1}H NMR. The number-average molecular weight (M_n) and polydispersity index (PDI) of $D_{2.0}$-*b*-PDMAEMA-Br were 4800 g mol^{-1} and 1.23, respectively, and those for $D_{2.0}$-*b*-PDMAEMA-*b*-PNIPAM were 7400 g mol^{-1} and 1.17, respectively.

2. Characterization

Molecular weights and polydispersity of the polymers were measured by a gel permeation

chromatograph (GPC) equipped with two Mixed-B columns (Polymer Laboratory Corp., pore size = 10 μm; column size = 300 × 7.5 mm) and a refractive index detector (Perkin-Elmer Series 200) using THF as the eluent at 30 ºC with a flow rate of 1 $mL \cdot min^{-1}$. The column system was calibrated by a set of mono-dispersed standard polystyrenes. ^{1}H NMR spectra were obtained on a 500 Bruker NMR instrument using D_2O as the solvent and TMS as a reference standard for chemical shifts.

3. The graft density of the modified Fe_3O_4 nanoparticles

The graft density of copolymers on the magnetic nanoparticles was determined according to the published document.[2] Briefly speaking, according to the density (ρ) of Fe_3O_4 (~5.18 g/cm^3), the diameter of the magnetic nanoparticles (~10 nm), and the obtained data of TGA and GPC from the Fe_3O_4-$D_{2.0}$-*b*-PDMAEMA-Br and Fe_3O_4-$D_{2.0}$-*b*-PDMAEMA-*b*-PNIPAM nanoparticles, the graft density (σ) can approximately be 0.56 and 0.50 chains/nm^2, respectively, which was calculated through the following relationship:

$$\sigma = \frac{d \cdot \omega \cdot N_A \cdot \rho}{6 \cdot M_w \left(1 - \omega\right)} \times 10^{-21}$$

Where d is the diameter of the magnetic nanoparticles, ω is the weight fraction loss of copolymer-modified nanoparticles, N_A is Avogadro constant, and M_w is the weight-average molecular weight of the copolymer.

4. The stability of Fe_3O_4 nanoparticles

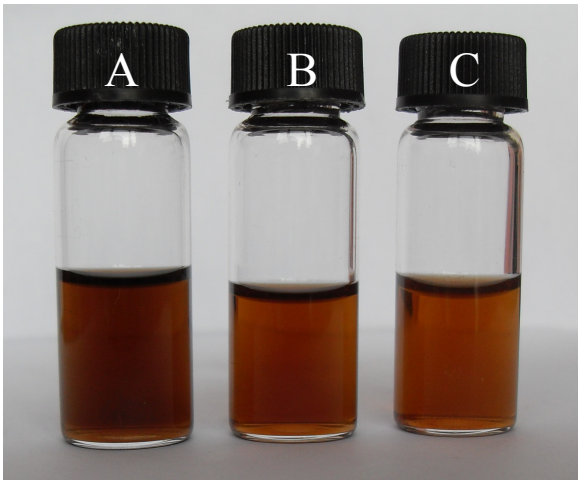

Figure S1

A, Fe_3O_4-ol in hexane (concentration: 1.2 mg/mL);

B, Fe_3O_4-$D_{2.0}$-*b*-PDMAEMA-*b*-PNIPAM in water for 2 months (concentration: 0.9 mg/mL);

C, Fe_3O_4-$D_{2.0}$-*b*-PDMAEMA-*b*-PNIPAM-crosslinked in water for 4 months (concentration:0.9 mg/mL)

5. GPC curves and ^{1}H NMR spectra of the functional copolymers

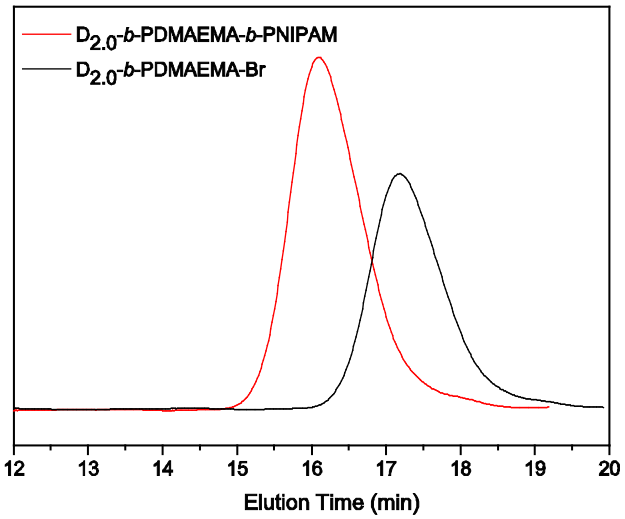

Figure S2 GPC curves of the functional copolymers

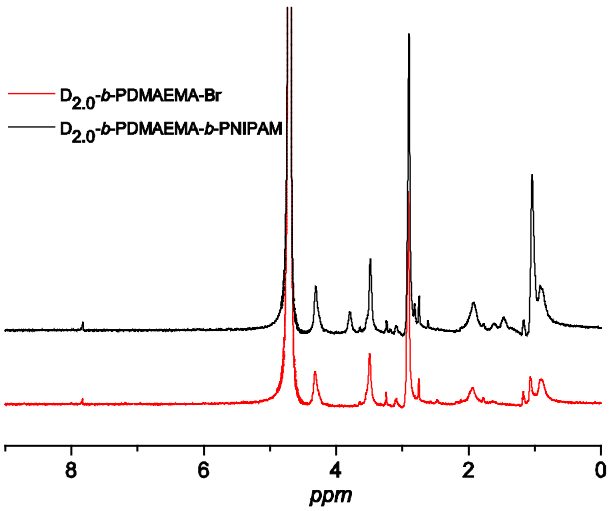

Figure S3 ^{1}H NMR spectra of the functional copolymers

Reference

1. C. Hua, S.-M. Peng and C.-M. Dong, *Macromolecules*, **2008,** 41, 6686-6695.

2. N. Dutta, D. Green, *Langmuir*, **2008,** 24, 5260-5269.