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Supporting Information:

Highly Water-Dispersed Superparamagnetic Magnetite Colloidal Nanocrystal Clusters From Multifunctional Polymeric Nanoreactors: Synthesis and Properties

Junjing Bai,[§] Xiaobing Wang,[§] Peng Fu, Zhe Cui,* Qingxiang Zhao,* Xinchang Pang,* and Minying Liu**

School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, China

*To whom correspondence should be addressed. [§]These authors contributed equally to this work.

Email: lmy@zzu.edu.cn, xinchang.pang@mse.gatech.edu, cuizhezzu@126.com, fupeng@zzu.edu.cn and zhaoqingxiang1@126.com

1. Experimental Section

1.1. Preparation of the Multi-arm Star-shaped Copolymers of [Poly (EO-*co*-EEGE)]$_{18}$ growing from α-CD as Core.[1]

The living anionic copolymerization of EO and EEGE was conducted in stainless steel kettle, using α-CD with 18 hydroxyl groups and DPMNa as co-initiator system. In a typical process, a 500 mL stainless steel kettle was dried by vacuuming at 50 °C for 6 h, and then cooled to -20 °C. Vacuum-dried α-CD (0.2g, 0.2mmol) was dissolved in 120 mL mixed solvent of anhydrous 1-methyl-2-pyrrolidione (NMP) and anhydrous THF (v/v=2/1), and then a THF soution of DPMNa (1.4mL, 0.51 M) was slowly added into reaction solution to form anionic initiators. Subsequently, the initiator solution was injected into the kettle, and then two monomers of EO (44.0g) and EEGE (29.2g) were also added. The living anionic copolymerization was carried out at 60 °C for 48 h, and then the polymerization was stopped by adding 4mL acidified methanol. When polymerization system was cooled to room temperature, the un-reacted monomers and solvent were removed by distillation under reduced pressure. The crude copolymers were purified by dissolving in 200 mL dichloromethane, and then washed with DI water. After dichloromethane was removed, transparent and yellowy viscous multi-arm star-shaped copolymers of [poly(EO-*co*-EEGE)]$_{18}$ was obtained. The molar ratio of EO to EEGE in the resulting star-shaped copolymers can be well adjusted by adjusting the feed molar ratio of EO to EEGE during the living anionic copolymerization process. In addition, the molecular weights of the resulting star-shaped copolymers can be also well tuned by changing the molar ratio of monomers to initiator.

1.2. Preparation of Star-shaped Block Copolymers of [Poly (EO-*co*-EEGE)-*b*-PEO]$_{18}$ by Using Multi-arm Star-shaped Copolymers of Poly (EO-*co*-EEGE) as Macroinitiators.

Similar with the synthesis process of multi-arm star-shaped copolymer [poly (EO-*co*-EEGE)]$_{18}$, multi-arm star-shaped block copolymers of [poly (EO-*co*-EEGE)-*b*-PEO]$_{18}$ were synthesized by anionic polymerization. In a typical process, a 500 mL stainless steel kettle was dried at 50 °C for 6 h under vacuum, and then cooled to -20 °C. Purified and dried multi-arm star-shaped [poly(EO-*co*-EEGE)]$_{18}$ (10.0g) was dissolved in 100 mL of mixture solvent of anhydrous DMSO and THF (v/v=3/2), and then the THF solution of DPMNa (4.8mL) was introduced into the solution to form macroinitiators. Sequentially, the macroinitiator solution and EO monomer (10.0g) were injected into polymerization reaction system. The polymerization process was carried out at 60°C for 48 h under stirring condition. The polymerization process was terminated by adding of 2mL acidified methanol. After the polymerization solution was concentrated by distillation under reduced pressure, the crude product was dissolved in 50 mL dichloromethane, and then precipitated in cold diethyl ether. The moleccular weight of PEO chains as shell can be well tuned by adjusting the molar ratio of EO to end hydroxyl groups of star-shaped macroinitiator during the polymerization process.

1.3. End-Capping Reaction of End Hydroxyl Groups of Star-shaped Block Copolymers of [Poly (EO-*co*-EEGE)-*b*-PEO]$_{18}$.

The end hydroxyl groups of arms of star-shaped block copolymers were end-capped by the reaction between hydroxyl groups and benzenecarbonyl chloride (end-capping reagent). In a typical process, star-shaped block copolymers of poly(EO-*co*-EEGE)-*b*-PEO (8.0 g) were dissolved in 100 mL anhydrous CH_2Cl_2, and then 2mL of triethylamine and benzenecarbonyl chloride (4.0g) was added into reaction solution at room temperature under stirring condition. The end-capping reaction was carried out at room temperature for 24h, and then then precipitated in cold diethyl ether. The resulting sample was purified by dissolution/precipitation with CH_2Cl_2/cold diethyl ether. The precipitate was dried in vacuum at 60 °C for 2h.

1.4. Synthesis of Water-Soluble Star-Shaped Block Copolymers of [Poly(EO-*co*-Gly)-*b*-PEO]$_{18}$ by Hydrolysis of the Ethoxyethyl Groups of EEGE units in Poly(EO-*co*-EEGE) Polymer Chains.

The cleavage reaction of ethoxyethyl groups was carried out according to literature.[2-4] Multi-arm star-shaped block copolymers of [poly(EO-*co*-EEGE)-*b*-PEO]$_{18}$ (2.0g) was added into 50 mL of formic acid. The reaction system solution was stirred at room temperature for 1h, and then removed formic acid by rotary evaporator. After that, the crude product was dissolved in a mixture of dioxane (40 mL) and methanol (20 mL), and hydrolysis reaction was carried out by adding KOH aqueous solution (1mol/L, 10 mL) under refluxing for 2h, and then neutralized with HCl aqueous solution (2 mol/L). All the solvents were removed under reduced pressure, the crude product was dissolved in water and purified by the dialysis. The purified aqueous solution was dried in vacuum at 80°C. The transparent viscous multi-arm star-shaped block copolymers of [poly(EO-*co*-Gly)-*b*-PEO]$_{18}$ was obtained.

1.5. Preparation of Star-Shaped Macroinitiators: Multi-Arm Star-Shaped Block Copolymers of [Poly(EO-*co*-BiBGE)-*b*-PEO]$_{18}$.

In a typical process, multi-arm star-shaped block copolymers of [poly(EO-*co*-Gly)-*b*-PEO]$_{18}$ (2.0g) was dissolved in 100 mL of anhydrous NMP, then 10.4 mL of 2-bromoisobutyryl bromide was introduced dropwise at 0 °C for 60 min under vigorous stirring. The reaction solution was stirred for 2 h at 0 °C, subsequently, stirring at room temperature for another 24 h. Then NMP was removed by by distillation under reduced pressure. The residue was dissolved in 50mL of CH_2Cl_2, and washed by NaOH aqueous solution (50mL, 1 mol/L), HCl aqueous solution (50mL, 1 mol/L), and DI water (50mL), respectively. After CH_2Cl_2 was removed by distillation in vacuum, the resulting multi-arm star-shaped block copolymer [poly(EO-*co*-2-bromoisobutyryloxyglycidyl ether)-*b*-PEO]$_{18}$ (poly(EO-*co*-BiBGE)-*b*-PEO) was dried in vacuum at 60°C for 4h.

2. Results and Discussion

2.1. Synthesis of Multi-Arm Star-Shaped Brush-Like Block Copolymer [(PEO-*g*-PAA)-*b*-PEO]$_{18}$.[1]

Firstly, multi-arm star-shaped copolymers of [poly(EO-*co*-EEGE)]$_{18}$ was synthesized by anionic copolymerization of EO and EEGE based on α-CD core. The glycidol (Gly) was protected with ethyl vinyl ether first to form EEGE monomer, and then was copolymerized with EO using a co-initiator system of α-CD and DPMNa. α-CD is a cyclic oligosaccharide consisting of six glucose units linked by α-1,4-glucosidic bonds.[5, 6] The 18 substitutable hydroxyl groups on the outer surface of α-CD provide the capability of making a core with 18 initiation sites to form 18-arm, star-shaped architectures. Four multi-arm star-shaped copolymers of [poly(EO-*co*-EEGE)]$_{18}$ with different molar ratio of EO and EEGE, and different arm length could be synthesized by adjusting the monomer feed molar ratio and the molar ratio of initiator to monomers as **Table S1**. GPC traces of the samples with monomodal traces were shown in **Figure S1**. The molecular weight of multi-arm star-shaped copolymers of [poly(EO-*co*-EEGE)]$_{18}$ can be tuned by changing the molar ratio of monomers to initiators.

Table S1. Summary of multi-arm star-shaped copolymers of [poly(EO-*co*-EEGE)]$_{18}$

Sample	R_f[a]	R_T[b]	$M_{n,\ GPC}$[c] (kg/mol)	PDI[d]	$M_{n,theory}$[e] (kg/mol)	$M_{n,arm}$[f] (kg/mol)	N_{EEGE}[g]
A-1	1/5	1/6.2	121.6	1.10	309.3	17.2	41
A-2	1/5	1/6.8	191.5	1.09	627.4	34.9	78
B-1	1/10	1/12.5	102.3	1.12	254.6	14.1	20
B-2	1/10	1/13.1	167.6	1.08	556.8	30.9	43

[a]The feed molar ratio of EEGE to EO. [b]The unit molar ratio of EEGE to EO in multi-arm star-shaped copolymers of [poly(EO-*co*-EEGE)]$_{18}$ measured by ^{1}H NMR. [c]Number-average molecular weight determined by GPC. [d]The polydispersity (PDI) determined by GPC. [e]The theoretical values of M_n calculated from the monomer conversion and the concentration of initiators. [f]Mn of each poly(EO-*co*-EEGE) arm calculated from the theoretical values of M_n. [g]The number of EEGE units in each arm of multi-arm star-shaped copolymers of [poly(EO-*co*-EEGE)]$_{18}$ calculated by the integration of protons from ^{1}H NMR.

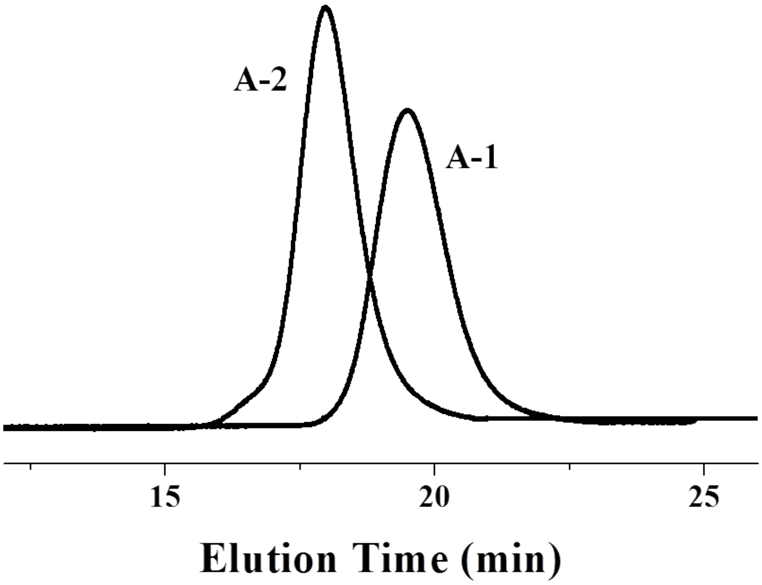


Figure S1. GPC traces of multi-arm star-shaped copolymers of [poly(EO-*co*-EEGE)]$_{18}$ (A-1 and A-2 samples were shown in **Table S1**).

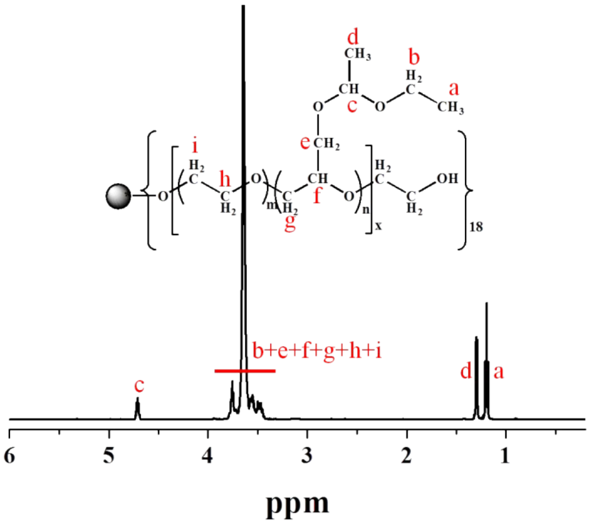


Figure S2. ^{1}H-NMR spectum of multi-arm star-shaped copolymers of [poly(EO-*co*-EEGE)]$_{18}$ (A-1 sample was shown in **Table S1**, solvent: $CDCl_3$).

The **Figure S2** shows a typical ^{1}H NMR spectrum of multi-arm star-shaped copolymers of [poly(EO-*co*-EEGE)]$_{18}$, the quadrilets at δ = 4.69-4.74 ppm are assigned to the methyl protons (H_c) of EEGE moiety, the doublets at δ = 1.30, 1.29 and the triplet at δ = 1.21, 1.19, 1.18 are assigned to methyl protons of EEGE moiety (H_d, H_a), the chemical shift at δ = 3.53-3.80 are assigned to protons of main chain ($H_{f,,}$ H_g, H_h, H_i) and protons of side chains ($H_{b,}$ H_e). The copolymer composition can be calculated by using following equation based on the ^{1}H NMR spectrum:

$$R_T = \frac{4A_c}{A_{sum} - 7A_c} \tag{S1}$$

Where R_T is the molar ratio of EEGE to EO in the resulting multi-arm star-shaped copolymers of [poly(EO-*co*-EEGE)]$_{18}$; A_{sum} and A_c represent the peak area sum of the protons (b+e+f+g+h+i) and the peak areas of the methine protons of the EEGE moiety, respectively. The R_T values of four samples were shown in **Table S1**, which is nearly equivalent to the monomer feed molar ratio of EEGE to EO. In addition, the average-number of the protected hydroxyls on each arm could be evaluated by the combination of the theoretical values of molecular weight of each arm and ^{1}H NMR spectrum using the following equation (S2):

$$N_{EEGE} = \frac{M_{n,arm}}{(146 + \frac{44}{R_T})} \qquad \text{(S2)}$$

in which $M_{n,arm}$ is the theoretical value of molecular weight of each arm, 146 and 44 are the molar masses of EEGE and EO, and R_T is the molar ratio of EEGE units to EO units in copolymers; all the N_{EEGE} values was listed in **Table S1**.

Sequential anionic polymerization strategy was used to polymerize monomer EO, the end hydroxyl groups of each arm of multi-arm star-shaped copolymers of [poly(EO-*co*-EEGE)]$_{18}$ and DPMNa exploited as macroinitiator system. The resulting multi-arm star-shaped block copolymers of [poly(EO-*co*-EEGE)-*b*-PEO]$_{18}$ samples were summarized in **Table S2**. After PEO chains growing from the end of poly(EO-*co*-EEGE) arm, obviously, molecular weight of each arm increased. In addition, according to GPC traces (**Figure S3**), the major elution peak of star-shaped block copolymer [poly(EO-*co*-EEGE)-*b*-PEO]$_{18}$ was shifted to the smaller elution time owing to the larger molecular weight. In addition, with the second block PEO capping on the first block poly(EO-*co*-EEGE), the obvious increase of the EO unit molar ratio in multi-arm star-shaped copolymers of [poly(EO-*co*-EEGE)]$_{18}$ demonstrates the successful growing of the second block PEO (**Figure S4**).

Table S2. Summary of multi-arm star-shaped block copolymers of [poly(EO-*co*-EEGE)-*b*-PEO]$_{18}$

Sample	R_T^b	$M_{n, GPC}^b$ (kg/mol)	PDI^c	$M_{n,arm}^d$ (kg/mol)
A-1a	1/9.3	153.1	1.15	5.6
A-2a	1/8.2	234.6	1.13	4.7
B-1a	1/19.8	131.9	1.18	6.3
B-2a	1/16.1	205.3	1.12	5.9

[a]The unit molar ratio of EEGE to EO in multi-arm star-shaped block copolymers of [poly(EO-*co*-EEGE)]$_{18}$ measured by ^{1}H NMR data. [b]Number-average molecular weight determined by GPC. [c]The polydispersity (PDI) determined by GPC. [d] Mn of each PEO block arm calculated from the monomer conversion and the concentration of initiators.

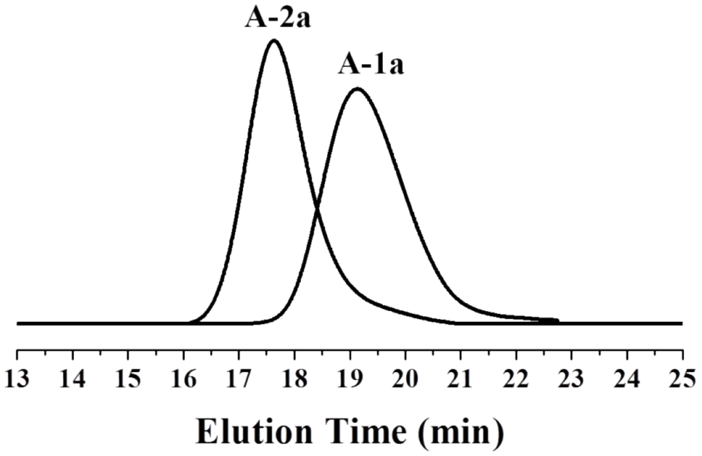


Figure S3. GPC traces of multi-arm star-shaped block copolymers of [poly(EO-*co*-EEGE)-*b*-PEO]$_{18}$ (A-1a and A-2a samples were shown in **Table S2**).

The end hydroxyl groups of multi-arm star-shaped block copolymers of [poly(EO-*co*-EEGE)-*b*-PEO]$_{18}$ were end-capped by the reaction between hydroxyl groups and benzenecarbonyl chloride as end-capping reagent. **Figure S4** shows the ^{1}H-NMR spectrum after the end-capping reaction, the appearance of chemical shift at δ =6.89-7.24 ppm is assigned to the protons of phenyl groups as end group of arm chains.

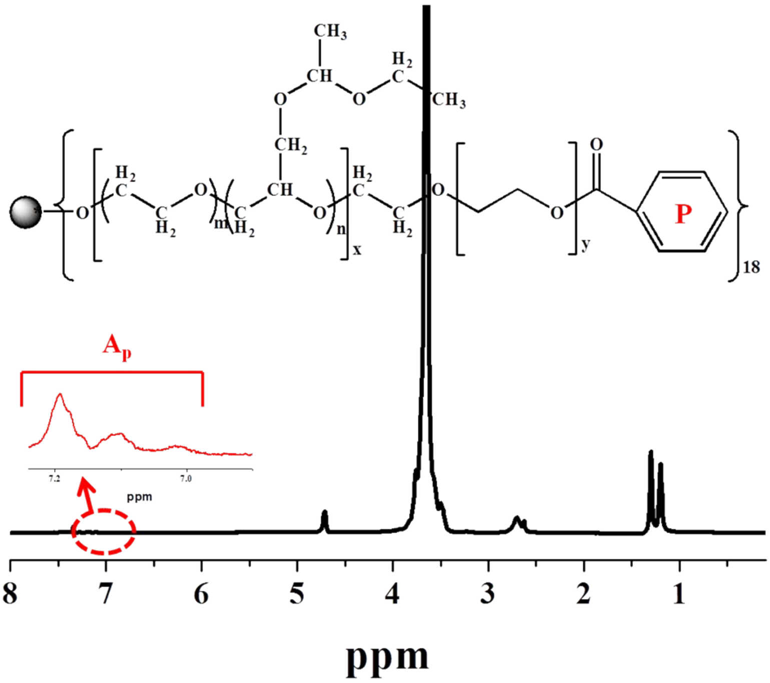


Figure S4. ^{1}H-NMR spectrum of multi-arm star-shaped block copolymers of [poly(EO-*co*-EEGE)-*b*-PEO]$_{18}$ after the end-capping reaction by benzenecarbonyl chloride (A-1a sample was shown in **Table S2**, solvent: $CDCl_3$).

To deprotect the reactive hydroxyl groups of multi-arm star-shaped block copolymers of [poly(EO-*co*-Gly)-*b*-PEO]$_{18}$, ethoxyethyl groups of EEGE units were hydrolyzed by the cleavage of the ethoxyethyl group. After hydroxyl groups were recovered, multi-arm star-shaped block copolymers of [poly(EO-*co*-EEGE)-*b*-PEO]$_{18}$ was transformed into multi-arm star-shaped block copolymers of [poly(EO-*co*-Gly)-*b*-PEO]$_{18}$ with multi-pending hydroxyl groups along the first block. The success of hydrolysis of the ethoxyethyl groups was confirmed by ^{1}H NMR characterization. All the peaks, which were assigned to the ethoxyethyl group of EEGE units in poly(EO-*co*-EEGE) block in **Figure S2**, disappeared completely after hydrolysis, as shown in **Figure S5**.

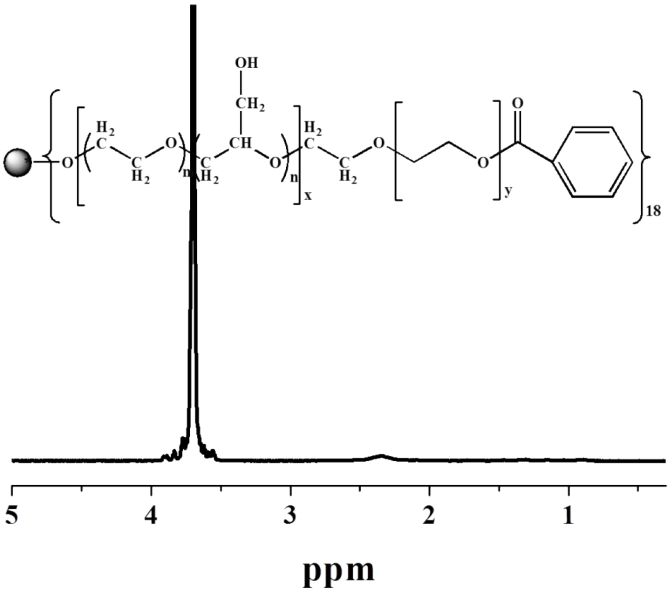


Figure S5. ^{1}H-NMR spectrum of multi-arm star-shaped block copolymers of [poly(EO-*co*-Gly)-*b*-PEO]$_{18}$ after the cleavage of the ethoxyethyl group (A-1a sample was used as the precursor in **Table S2**, solvent: $CDCl_3$).

In order to prepare star-shaped brush-like macroinitator, multi-arm star-shaped block copolymers of [poly(EO-*co*-BiBGE)-*b*-PEO]$_{18}$, the hydroxyl groups of multi-arm star-shaped block copolymers of [poly(EO-*co*-Gly)-*b*-PEO]$_{18}$ were modified by the esterification with 2-bromoisobutyryl bromide. The successful esterification of the hydroxyl groups was also confirmed by ^{1}H NMR shown in **Figure S6**, in which the appearance of new peaks at δ=1.8-2.2 and δ=4.13-4.42 can be assigned to the methyl protons of ATRP initiating sites and the protons (H_e) linked to the ester, respectively.

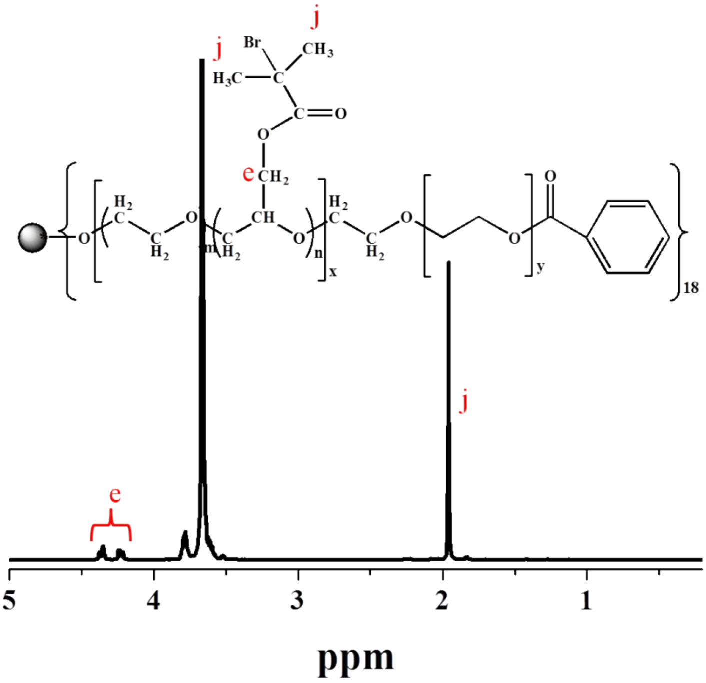


Figure S6. ^{1}H-NMR spectrum of multi-arm star-shaped block copolymers of [poly(EO-*co*-BiBGE)-*b*-PEO]$_{18}$ after the esterification with 2-bromoisobutyryl bromide of star-shaped block copolymers of [poly(EO-*co*-Gly)-*b*-PEO]$_{18}$ (A-1a sample was used as the precursor in **Table S2**, solvent: $CDCl_3$).

In order to confirm that the star-shaped structures survives after hydrolysis of the ethoxyethyl groups of poly(EO-*co*-EEGE)-*b*-PEO arms, macroinitiator multi-arm star-shaped block copolymer poly(EO-*co*-BiBGE)-*b*-PEO for ATRP was also characterized by GPC. Comparing with GPC trace of corresponding multi-arm star-shaped block copolymers of poly(EO-*co*-EEGE)-*b*-PEO (Sample A-1a in Table S2, M_n=153.1kg/mol, PDI=1.15), the major elution peak of macroinitiator multi-arm star-shaped block copolymer poly(EO-*co*-BiBGE)-*b*-PEO for ATRP (M_n=176.8kg/mol, PDI=1.08) was shifted to the slightly smaller elution time owing to the modification of hydroxyl groups by 2-bromoisobutyryl bromide (larger molecular weight than ethoxyethyl groups).

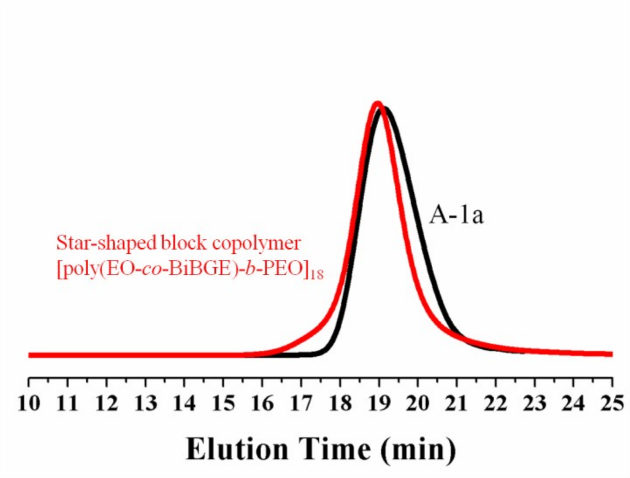


Figure S7. Comparison of GPC traces of multi-arm star-shaped block copolymers of [poly(EO-*co*-EEGE)-*b*-PEO]$_{18}$ (A-1a sample was shown in **Table S2**) and its corresponding ATRP macroinitiator of multi-arm star-shaped block copolymer poly(EO-*co*-BiBGE)-*b*-PEO.

The ATRP of *t*BA monomer was carried out in acetone at 60 °C, multi-arm star-shaped block copolymers of [poly(EO-*co*-BiBGE)-*b*-PEO]$_{18}$ as the macroinitiator, the PMDETA/CuBr as catalyst system. The resulting multi-arm star-shaped brush-like block copolymers consist of PEO as main chain, P*t*BA as graft chains and the second PEO block as shell. Four multi-arm star-shaped brush-like block copolymers of [(PEO-g-P*t*BA)-*b*-PEO]$_{18}$ samples were prepared by using four corresponding star-shaped brush-like macroinitators with different bromoisobutyryl groups density, and all the results were shown in **Table S3**. **Figure S8** shows GPC traces of two multi-arm star-shaped brush-like block copolymers of [(PEO-g-P*t*BA)-*b*-PEO]$_{18}$ samples.

All the star-shaped brush-like copolymers with symmetric GPC peaks were obtained no matter what star-shaped brush-like ATRP macroinitators were used. In addition, and the narrow molecular weight distribution of the star-shaped polymeric brushes as low as 1.15 demonstrates that all the samples have uniform molecular weights. **Figure S9** showed the ^{1}H NMR spectrum of the resultant multi-arm star-shaped brush-like block copolymers of [(PEO-g-P*t*BA)-*b*-PEO]$_{18}$ sample A-1b in **Table S3**. The peaks at δ = 4.05-4.40 ppm were assigned to the methylene protons (H_e) linked to ester and end methine protons at the ω-end of the copolymer side chains. A characteristic strong peak at 1.45 ppm corresponding to the methyl protons in *t*-butyl group of *t*BA unit, and the chemical shift at δ =3.46-3.75 ppm represent the protons of PEO backbone. In addition, the molecular weight of P*t*BA grafting side chains can be obtained by equation (S3):

$$M_{n,PtBA} = \frac{\frac{A_k}{9}}{\frac{A_j}{6}} \times 128.17 \qquad \text{(S3)}$$

where $M_{n,PtBA}$ is the molecular weight of P*t*BA grafting side chains shown in **Table S3**, A_k and A_j represented the integral area of the methyl protons in *t*-butyl group of the grafted P*t*BA chains and the integral area of methyl protons at the α-end of the P*t*BA side chains, respectively. 128.17 is the molar mass of *t*BA monomer.

Table S3. Summary of multi-arm star-shaped brush-like copolymers of [(PEO-*g*-P*t*BA)-*b*-PEO]$_{18}$

Sample	$M_{n,\ GPC}$[a] (kg/mol)	PDI[b]	$M_{n,PtBA}$[c] (kg/mol)
A-1b	218.5	1.12	4.2
A-2b	321.3	1.15	4.9
B-1b	179.5	1.14	4.6
B-2b	268.9	1.10	5.1

[a]Number-average molecular weight determined by GPC. [b]The polydispersity (PDI) determined by GPC. [c]Mn of each P*t*BA graft chain calculated from ^{1}H-NMR data.

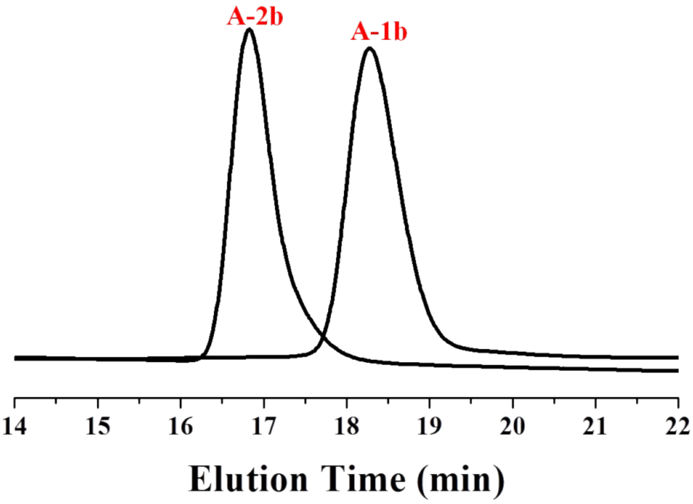


Figure S8. GPC traces of multi-arm star-shaped brush-like block copolymers of [(PEO-g-P*t*BA)-*b*-PEO]$_{18}$ (A-1b and A-2b samples were shown in **Table S3 (Table 1)**).

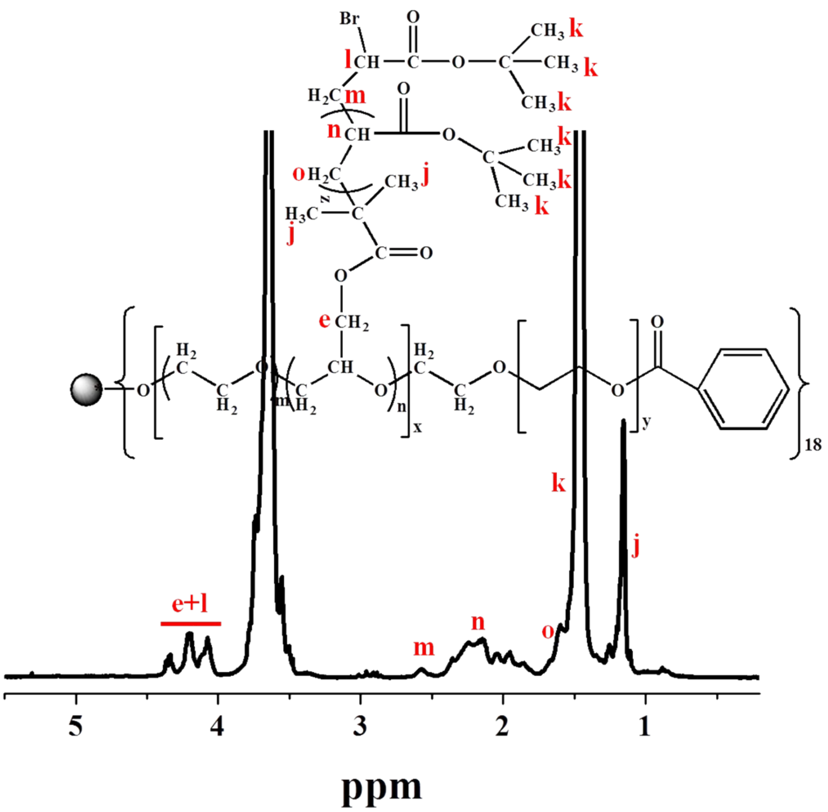


Figure S9. ^{1}H-NMR spectrum of multi-arm star-shaped brush-like block copolymers of [(PEO-g-P*t*BA)-*b*-PEO]$_{18}$ (A-1b sample in **Table S3 (Table 1)**, solvent: $CDCl_3$).

Finally, the water-soluble multi-arm star-shaped brush-like block copolymer [(PEO-*g*-PAA)-*b*-PEO]$_{18}$ was prepared by the hydrolysis of the *t*-butyl groups of P*t*BA grafted side chains in trifluoroacetic acid. The characterization spectrum of water-soluble multi-arm star-shaped brush-like block copolymer was shown in **Figure S10**. The complete disappearance of the chemical shift at 1.45 ppm corresponding to the methyl protons of the *t*-butyl groups demonstrated the successful hydrolysis of P*t*BA grafting chains. In addition, FT-IR analysis was used to confirm the successful hydrolysis of the *t*-butyl groups. As shown in **Figure S11**, the broad absorbance characteristic of a carboxylic acid group appeared at 2800-3600 cm^{-1} and the carbonyl stretch had shifted from 1726 to 1700 cm^{-1}.

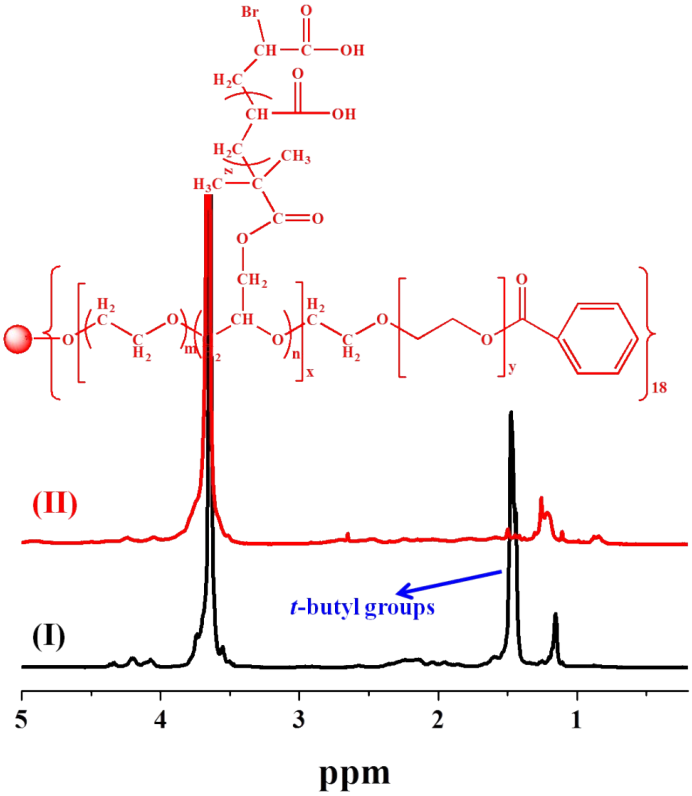


Figure S10. ^{1}H NMR spectra of multi-arm star-shaped brush-like block copolymers (I) [(PEO-*g*-P*t*BA)-*b*-PEO]$_{18}$ (Sample A-1b in **Table S3 (Table 1)**) in $CDCl_3$ and (II) the resulting [(PEO-*g*-PAA)-*b*-PEO]$_{18}$ in CD_3OD.

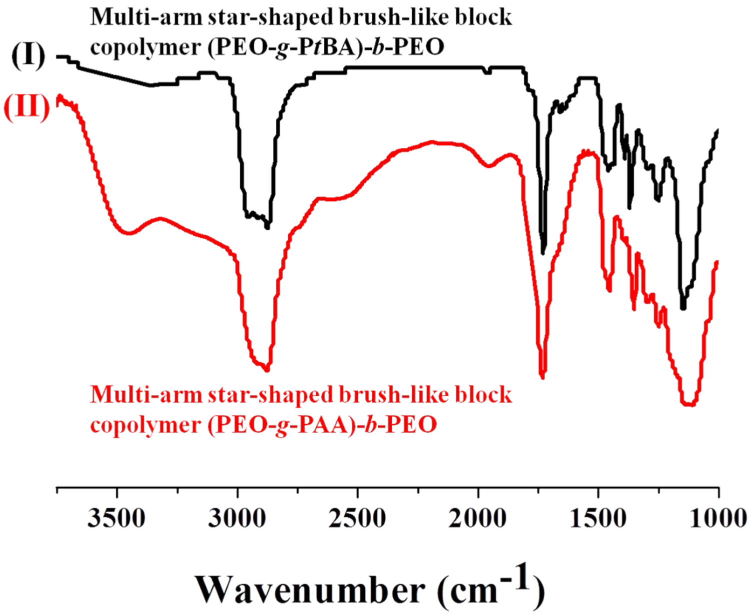


Figure S11. FT-IR spectra of multi-arm star-shaped brush-like block copolymers (I) [(PEO-*g*-P*t*BA)-*b*-PEO]$_{18}$ (Sample A-1b in **Table S3 (Table 1)**) and (II) the corresponding [(PEO-*g*-PAA)-*b*-PEO]$_{18}$.

2.2. Fabrication of Superparamagnetic Fe_3O_4 Colloidal Nanocrystal Clusters Capped with PEO as Hydrophilic Shell.

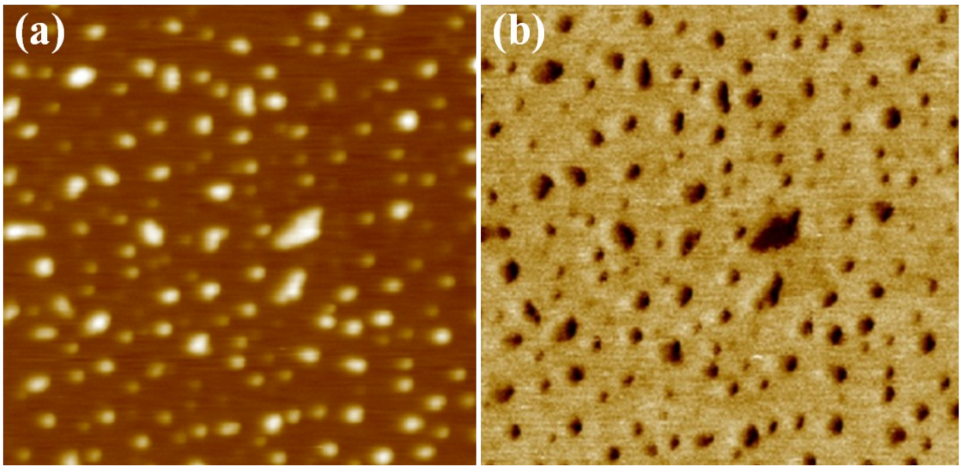


Figure S12. AFM height and phase images of the water-soluble multi-arm star-shaped brush-like block copolymer [(PEO-*g*-PAA)-*b*-PEO]$_{18}$ (Sample A-1b as precursor in **Table S3 (Table 1)**), respectively. image size= 2.5×2.5μm^2, Z range= 30nm for (a) and 88^o for (b).

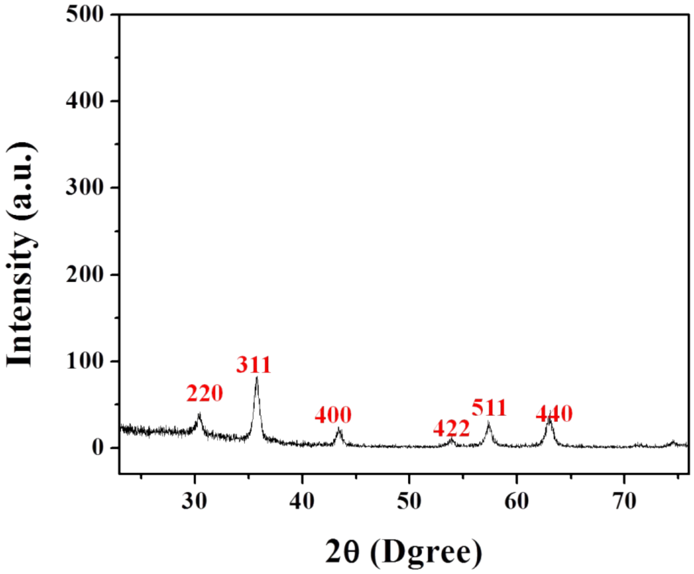
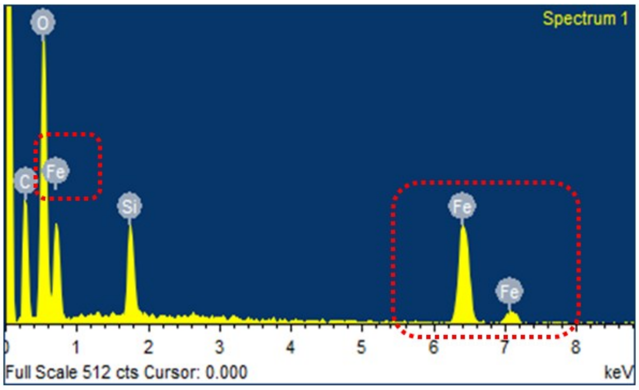


Figure S13. XRD pattern of Fe_3O_4 colloidal nanocrystal clusters by using the water-soluble multi-arm star-shaped brush-like block copolymer [(PEO-*g*-PAA)-*b*-PEO]$_{18}$ (Sample A-1b as precursor in **Table S3 (Table 1)**) as multifunctional polymeric nanoreactor.



Element	Weight%	Atomic%
C K	26.59	43.34
O K	33.71	41.24
Si K	4.34	3.03
Fe K	35.36	12.39
Totals	100.00	

Figure S14. EDS spectrum of Fe_3O_4 colloidal nanocrystal clusters by using the water-soluble multi-arm star-shaped brush-like block copolymer [(PEO-*g*-PAA)-*b*-PEO]$_{18}$ (Sample A-1b as precursor in **Table S3 (Table 1)**) as multifunctional polymeric nanoreactor.

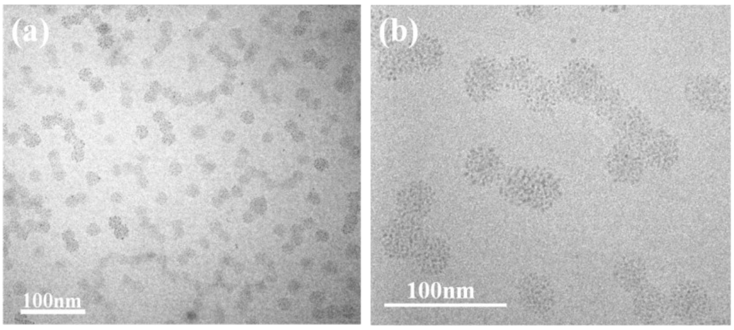


Figure S15. TEM images of Fe_3O_4 colloidal nanocrystal clusters after six cycles of magnetic sequestration/redispersion (the sample shown in **Figure 5(b)**).

References

1. J. Bai, X. Wang, P. Fu, Z. Cui, Q. Zhao, X. Pang and M. Liu, *RSC Adv.*, 2015, **5**, 96785-96798.
2. D. Taton, A. Le Borgne, M. Sepulchre and N. Spassky, *Macromol. Chem. Phys.*, 1994, **195**, 139-148.
3. P. Li, Z. Li and J. Huang, *Macromolecules*, 2007, **40**, 491-498.
4. Z. Li, P. Li and J. Huang, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 4361-4371.
5. Z. Liu, M. Frasconi, J. Lei, Z. J. Brown, Z. Zhu, D. Cao, J. Iehl, G. Liu, A. C. Fahrenbach, Y. Y. Botros, O. K. Farha, J. T. Hupp, C. A. Mirkin and J. Fraser Stoddart, *Nat. Commun.*, 2013, **4**, 1855.
6. I. Tomatsu, A. Hashidzume and A. Harada, *J. Am. Chem. Soc.*, 2006, **128**, 2226-2227.