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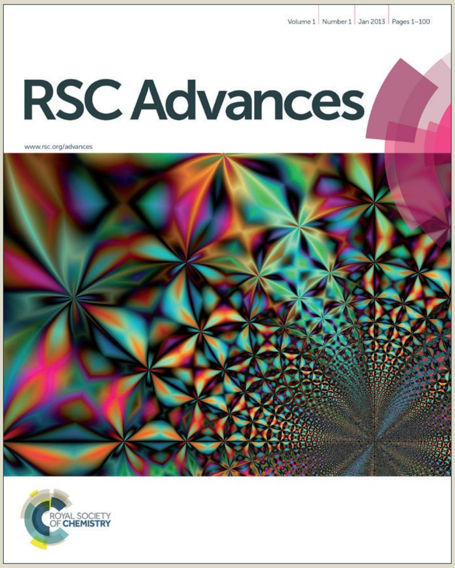

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# Water-soluble Star-Shaped Brush-Like Block Copolymers: Synthesis and Application as Multicompartment Nanoreactors for Fabrication of Quantum Dot Colloidal Nanocrystal Clusters

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## Abstract:

A series of novel water-soluble multi-arm star-shaped brush-like block copolymers, composed of poly(ethylene oxide)(PEO) as main chain, poly(acrylic acid) (PAA) as functional graft chains, and the second PEO block as shell (i.e., multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO) with different molecular weights and grafting density, were rationally designed and synthesized by a combination of anionic copolymerization and atom transfer radical polymerization (ATRP). The anionic ring-opening copolymerization of ethylene oxide (EO) and ethoxyethyl glycidyl ether (EEGE) was conducted first by using α-cyclodextrin (α-CD) with 18 hydroxyl groups and diphenylmethyl sodium

(DPMNa) as co-initiator system. The monomer reactivity ratios for EO and EEGE were also determined: $r_{1(EO)}$=1.18±0.03 and $r_{2(EEGE)}$=0.79±0.01, respectively. Then the resulting multi-arm star-shaped copolymers of poly(EO-*co*-EEGE) with hydroxyls as end functional groups were utilized as star-shaped macroinitiators to sequentially initiate the anionic ring-opening polymerization of monomer EO for the second block hydrophilic homopolymer PEO chain growing on the first block poly(EO-*co*-EEGE) arm end, and then ethoxyethyl groups of star-shaped block copolymers of poly(EO-*co*-EEGE)-*b*-PEO obtained were removed by hydrolysis. The forming multi-arm star-shaped block copolymers of EO and glycidol (Gly) with multi-pendant hydroxymethyls (star-shaped block copolymer poly(EO-*co*-Gly)-*b*-PEO) was then esterified by the reaction of pending hydroxyl groups of glycidol units of copolymers with 2-bromoisobutyryl bromide, and the resulting star-shaped brush-like macroinitiators were used to initiate the grafting polymerization of *t*-butyl acrylate (*t*BA) by ATRP technique. Finally, the *tert*-butyl ester groups of P*t*BA grafting side chains were selectively hydrolyzed in trifluoroacetic acid to obtain the water-soluble multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO). The water-soluble star-shaped brush-like (PEO-*g*-PAA)-*b*-PEO, consisted of funcitonal PAA domain as core and hydrophilic PEO domain as shell, were exploited as polymeric nanoreactors to structure-direct in situ fabrication of CdSe quantum dots (QDs) colloidal nanocrystal clusters composed of primary CdSe nanocrystals as subunits, the secondary structures of CdSe nanocrystals. Spherical CdSe colloidal nanocrystal clusters were intimately and permanently capped with hydrophilic PEO

chains on the surface to render the resulting clusters with highly water dispersible property.

**Keyword:** star-shaped brush-like block copolymers; controlled/living polymerization techniques; multicompartment polymeric nanoreactors; hybrid inorganic-organic core-shell colloidal nanocrystal clusters; highly water-dispersed quantum dots

## Introduction

When two or more different hydrophilic polymer segments were organized into one copolymer architecture, a class of copolymers, double-hydrophilic copolymers were formed.[1] Owing to some special properties, such as polarity transformation with changing pH or temperature, interaction with metal ions, solid substrates, colloids and biomolecules, etc., synthesis of these copolymers was also paid much attention. The typical hydrophilic segments include poly(ethylene oxide)(PEO), poly(acrylic acid)(PAA), poly(vinyl pyridine), poly(*N,N′*-dimethyl aminoethyl methacrylate), poly(*N*-isopropylacrylamide), etc.[2-5] Especially for hydrophilic PEO and PAA segments: PEO segments are not only hydrophilic, but also nonionic and crystalline, and PAA as a sort of hydrophilic weak polyelectrolyte, in which the degree of ionization is controlled by the pH values and the ionic strength of the aqueous solution,[6] can be used for the interaction of PAA segments with metal ions.[7-9] The copolymers with different structures comprising such hydrophilic segments have been applied in many fields, such as reverse-assembly,[5] stabilization of inorganic particles,[10] crystal growth modifiers,[11] drug carriers[12] and gene therapies.[13]

Star-shaped polymers comprising more than three linear polymer chains covalently joined to a core have the simplest structure in numerous possible branched topologies.[14-17] Owing to their compact architectures (i.e., smaller hydrodynamic volume and radius of gyration), globular shapes, and high concentration of terminal functional groups, comparing with the linear analogues of identical molar mass, star-shaped polymers exhibit high solubility in common solvents, low viscosity, and modified thermal properties.[18-21]As such, star-shaped polymeric architectures provide most of the properties of high molecular weight materials without the solution viscosity penalty of linear polymers of similar molecular weight for potential applications in coatings, additives, drug and gene delivery, and supramolecular science.[22-26] In addition, copolymer brushes composed of a flexible linear backbone and densely grafted side chains are an unique class of copolymers with intriguing structures, and can be prepared by different approaches: “grafting onto”, “grafting through” and “grafting from”.[27] Due to the distinctive chemical and physical properties originating from their intrinsically complex architectures, copolymer brushes have received much attention to investigate the structure-property relationship[27, 28] for potential applications in supramolecular science, biomaterials, advanced materials,[29] photonic crystals,[30] etc.

With the development in controlled/living polymerization techniques, such as living anionic polymerization, controlled radical polymerization (e.g., atom transfer radical polymerization (ATRP)),[21, 31-33] functional copolymers with well-defined yet complex architectures can be rationally designed and synthesized, such as multicomponent bottlebrush copolymers, [34] coil-rod brush copolymers, [35] star-like block copolymers, [36] four-arm star molecular brushes, [37, 38] etc. However, it is notewhorthy that these copolymers have linear polymeric brush structures, or the number of arms of star molecular brushes was rarely larger than four, or these polymeric architectures aren't double-hydrophilic. In order to prepare star-shaped polymeric structures, the arm-first strategy or the core-first strategy was usually used.[39, 40] In the arm-first method, the linear arms are prepared first, followed by connecting the arms to the core. The connection of arms is obtained by using either a difunctional monomer or a multifunctional terminating agent. When a difunctional monomer was used as a cross-linking agent to form star-shaped structures, the number of arms in these star-shaped polymers is difficult to be precisely controlled, especially for linear copolymer brushes as arms with strong steric hindrance effect. If star-shaped structures (especially linear copolymer brushes as arms) are synthesized by grafting onto a core having multifunctional terminating groups, the main problem is steric hindrance to lead to the difficulty of reaction between the linear polymer arm end and the multifunctional coupling agent. Comparing with the arm-first strategy, in the core-first method, star-shaped structures are prepared by using a multifunctional initiator as the core to initiate the growth of arms by the monomer addition. The main difficulty is choice of multifunctional initiators with precise initiating sites, well-defined structures and combined ability of forming star-shaped structures and brush-like structures. So it is still a challenge to assembly more linear copolymer brushes as arms with two functional hydrophilic segments into star-shaped structures.

The macromolecule micelles from linear amphiphilic block copolymers have been used as soft templates to stabilize inorganic nanocrystals for a long time. For example, amphiphilic block copolymers, polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP), have been utilized as soft templates to fabricate a series of nanocrystals (e.g., Au, Ag and Pt, etc.).[41, 42] However, these macromolecular micelles as templates by aggregates of conventional linear amphiphilic block copolymers were formed above their critical micelle concentration,[43-45] and their characteristics in a given system depend heavily on the thermodynamic properties of the solvent and on temperature. The shapes and structures of the micelles can change with varying ambient conditions, such as solvent, concentration, pH, temperature and so on.[21] In contrast, dendritic or star-shaped macromolecules with compact structures form macromolecular architectures, in which different functional polymeric segments are covalently linked to small molecule cores. So these polymeric architectures are static and structurally stable.[46, 47]

In this contribution, a series of novel water-soluble multi-arm star-shaped brush-like block copolymers, composed of poly(ethylene oxide)(PEO) as main chain, poly(acrylic acid) (PAA) as functional graft chains, and the second PEO block as shell (i.e., multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO) with different molecular weights and grafting density, were rationally designed and synthesized via a combination of anionic copolymerization and atom transfer radical polymerization (ATRP). The anionic ring-opening copolymerization of ethylene oxide (EO) and ethoxyethyl glycidyl ether (EEGE) was conducted first by using α-cyclodextrin (α-CD) with 18 hydroxyl groups and diphenylmethyl sodium (DPMNa) as co-initiator system. The monomer reactivity ratios for EO and EEGE were also determined: $r_{1(EO)}=1.18\pm0.03$ and $r_{2(EEGE)}=0.79\pm0.01$, respectively. Then the resulting multi-arm star-shaped copolymers of poly(EO-*co*-EEGE) with hydroxyls as end functional groups were utilized as star-shaped macroinitiators to sequentially initiate the anionic ring-opening polymerization of monomer EO for the second block hydrophilic homopolymer PEO chain growing on the first block poly(EO-*co*-EEGE) arm end, and then ethoxyethyl groups of star-shaped block copolymers of poly(EO-*co*-EEGE)-*b*-PEO obtained were removed by hydrolysis. The forming multi-arm star-shaped block copolymers of EO and glycidol (Gly) with multi-pendant hydroxymethyls (star-shaped block copolymer poly(EO-*co*-Gly)-*b*-PEO) was then esterified by the reaction of pending hydroxyl groups of glycidol units of copolymers with 2-bromoisobutyryl bromide, and the resulting star-shaped brush-like macroinitiators were used to initiate the grafting copolymerization of *t*-butyl acrylate (*t*BA) by ATRP technique. Finally, the *tert*-butyl ester groups of P*t*BA as grafting side chains were selectively hydrolyzed in trifluoroacetic acid to obtain the water-soluble multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO). The water-soluble star-shaped brush-like (PEO-*g*-PAA)-*b*-PEO, consisted of funcitonal PAA domain as core and hydrophilic PEO domain as shell, were exploited as polymeric nanoreactors to structure-direct in situ fabrication of CdSe quantum dots (QDs) colloidal nanocrystal clusters composed of primary CdSe nanocrystals as subunits, the secondary structures of CdSe nanocrystals. Spherical CdSe colloidal nanocrystal clusters were intimately and permanently capped with hydrophilic PEO chains on the surface to render the resulting clusters with highly water dispersible property.

## Experimental Section

### Materials.

Ethylene oxide (EO, ≥99.5%), α-cyclodextrin (α-CD, ≥99%), *N,N,N′,N″,N″*-pentamethyldiethylene triamine (PMDETA, 99%), 1-methyl-2-pyrrolidinone (NMP, anhydrous, 99.5%), benzenecarbonyl chloride (≥99.0%) and trifluoroacetic acid (TFA, 99%) were purchased from Sigma-Aldrich, and used as received. CuBr (98%, Sigma-Aldrich) was stirred for 24h in acetic acid, filtered, washed with ethanol and diethyl ether successively, and dried in vacuum. *tert*-Butyl acrylate (*t*BA, Sigma-Aldrich 98%), methyl ethyl ketone (99.9%, Fisher Scientific) and *N,N*-dimethylformamide (DMF, Fisher Scientific, 99.9%) were dried over $CaH_2$ and distilled under reduced pressure prior to use. Diphenylmethyl sodium (DPMNa) ($c$=0.51 M) was prepared according to the literature.[48] Tetrahydrofuran (THF, 99%, BDH) was dried by refluxing over sodium, and then distilled from sodium naphthalenide solution. Ethoxyethyl glycidyl ether (EEGE) was prepared by protecting the hydroxyl group of glycidol (Gly) with ethyl vinyl ether according to previously reported procedure.[48] Cadmium acetylacetonate ($Cd(acac)_2$, ≥99.9%), selenium powder (Se, 99.99%) and sodium borohydride ($NaBH_4$, ≥99%) were purchased from Sigma-Aldrich and used as starting materials without further purification. All other reagents were purified by common purification procedures.

### Characterizations.

Molecular weights of copolymers were characterized by gel permeation chromatography (GPC, Agilent1100) equipped with a G1310A pump, a G1362A refractive detector and a G1314A variable wavelength detector. THF was used as as the mobile phase at the flow rate of 1.0 mL/min at 35°C. One LP 5 μm gel column and two 5 μm gel LP mixed bed column were calibrated with 10 polystyrene (PS) standard samples with molecular weights ranging from 200 to $3\times10^6$ g/mol. GPC characterizations of multi-arm star-shaped block copolymers of poly(EO-*co*-Gly)-*b*-PEO were performed by gel permeation chromatography (GPC, Agilent1100) equipped with a G1315A diode-array detector. Aqueous $NaNO_3$ (0.1 M) was used as as the mobile phase at 40 °C with an elution rate of 0.5 mL/min. Three TSK-gel PW columns in series (bead size: 6, 13, 13 $\mu$m; pore size: 200 Å, greater than 1000 Å, less than 100-1000 Å; molecular range: $0\text{-}5\times10^4$, $5\times10^4\text{-}8\times10^6$, $(5\text{-}8)\times10^6$ g/mol, respectively) were calibrated by standard samples (linear PEO). $^1$H nuclear magnetic resonance ($^1$H-NMR) spectra were obtained using a Bruker 400 MHz spectrometer with the solvent resonances with tetramethylsilane (TMS) as the internal standard. $CDCl_3$ and methanol-$d_4$ ($CD_3OD$) were used as the solvent. FTIR spectra were obtained on a Magna-550 Fourier transform infrared spectrometer. Morphology of star-shaped brush-like (PEO-*g*-PAA)-*b*-PEO polymeric nanoreactors and resulting colloidal $Fe_3O_4$ nanocrystal clusters were characterized by transmission electron microscope (JEOL 1200EX TEM; operated at 80 kV). TEM samples of template copolymers were prepared by applying a drop of star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO DMF solution (~5 μL at c=1 mg/mL) onto a carbon coated copper TEM grid (300 mesh) and allowing DMF to evaporate in a vacuum oven at room temperature. Then the copolymer samples were stained with uranyl acetate. A droplet of freshly prepared saturated uranyl acetate aqueous solution (~20 μL) was deposited onto dried TEM samples.[49, 50] The excess solution was removed using a filter paper after 5 min. For TEM characterization of star-shaped brush-like block copolymer (PEO-*g*-P*t*BA)-*b*-PEO, TEM samples were prepared by using a drop of star-shaped copolymers dichloromethane ($CH_2Cl_2$) solution (c=1mg/mL) onto a carbon-coated copper TEM grid (300 mesh) and leaving $CH_2Cl_2$ to completely evaporate at room temperature, and then the TEM grid was exposed to vapors of ruthenium tetraoxide ($RuO_4$) with which the PEO and P*t*BA blocks were stained.[51-53] Morphologies of multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO were measured by atomic force microscopy (AFM, Bruker Dimension 3000) in the tapping mode. AFM characterization samples were prepared by spin-coating the DMF solution (c=1 mg/mL) on a silicon substrate at 2000 rpm for 1 min. Dynamic light scattering (DLS) data was acquired by laser light scattering spectrometer (Malvern Autosizer 4700) at 25°C. The crystalline structures of samples were measured by X-ray diffraction (XRD; SCINTAG XDS-2000, Cu Kα radiation). The energy dispersive spectroscopy (EDS) microanalysis of samples was conducted by field emission scanning electron microscopy (FE-SEM; FEI Quanta 250). The absorption spectra were recorded with a UV-Vis spectrometer (UV-2600, Shimadzu). The emission spectra were obtained by a spectrofluorophotometer (RF-5301PC, Shimadzu), and all samples were excited at $\lambda_{ex}$ = 350 nm.

### Synthesis of the Star-shaped Copolymers Poly (EO-*co*-EEGE) Based on α-CD.

The copolymerization of two monomers (EO and EEGE) was carried out in stainless steel kettle, α-CD with 18 hydroxyl groups and DPMNa as co-initiator system. In a typical process for the preparation of multi-arm star-shaped copolymers, a 200 mL stainless steel kettle was vacuumed at 60 °C for 5 h, and then cooled to -30 °C. α-CD (0.1g, 0.1mmol), vacuum-dried at 80 $^{o}$C overnight, was dissolved in 60 mL anhydrous mixed solvent of 1-methyl-2-pyrrolidione (NMP) and THF (v/v=2/1), and then a THF DPMNa solution (1.8mL, 0.51 M) was slowly introduced into reaction system. With the alkoxides forming under stirring, the color of homogeneous initiator system was changed to yellow. After that, the initiator solution was added into the reaction kettle, sequentially, two monomers: EO (22.0g, 0.5mol) and EEGE (14.6g, 0.1mol) were introduced. The anionic polymerization reaction was allowed to continue at 60 °C for 48 h, and then the anionic polymerization was terminated by adding of 2mL acidified methanol. All the solvents and un-reacted monomers were removed by distillation under reduced pressure. The crude copolymers were dissolved in 100 mL dichloromethane, and then washed with DI water. After removal of dichloromethane solvent, transparent and yellowy viscous multi-arm star-shaped copolymers poly(EO-*co*-EEGE) was obtained. The molar ratio of EO to EEGE in the star-shaped copolymers can be well tuned by adjusting the feed molar ratio of EO to EEGE during the anionic copolymerization process. In addition, samples with different molecular weight can be prepared by changing the molar ratio of initiator to monomers.

### Measurement of Reactivity Ratios of Two Monomers: EO and EEGE. [54]

Reactivity ratios of two Monomers (EO and EEGE) were determined according to YBR method during the anionic copolymerization. [54] The anionic copolymerization of two monomers (EO and EEGE) with different feed molar ratio was performed under the same reaction conditions of the synthesis of multi-arm star-shaped copolymers poly(EO-*co*-EEGE). The anionic copolymerization reactions were stopped at below 10% monomer conversion. After copolymerization reaction for 1h, all the solvents and residual monomers were removed by vacuum distillation, all the products were purified and dried, then structure and composition were determined by $^1$H NMR. The reactivity ratios were calculated by the equation (1):

$$\left(\frac{x}{\sqrt{y}}\right)r_1-\left(\frac{\sqrt{y}}{x}\right)r_2+\left(\frac{1}{\sqrt{y}}-\sqrt{y}\right)=0 \qquad (1)$$

Where $x$ is the feed molar ratio of EO to EEGE, $y$ is the molar ratio of EO to EEGE in the resulting copolymer. $r_1$ and $r_2$ are reactivity ratios of EO and EEGE, respectively.

**Synthesis of Star-shaped Block Copolymers Poly (EO-*co*-EEGE)-*b*-PEO**.

Similar with the synthesis procedure of star-shaped copolymers poly (EO-*co*-EEGE), multi-arm star-shaped block copolymers poly (EO-*co*-EEGE)-*b*-PEO were prepared by sequential anionic polymerization, star-shaped copolymers poly (EO-*co*-EEGE) with end hydroxyl groups and DPMNa as co-initiator system. The anionic polymerization of monomer EO was carried out in stainless steel kettle. In a typical polymerization process, a 200 mL stainless steel kettle was dried at 60 °C for 5 h under vacuum, and then cooled to -30 °C. Vacuum-dried multi-arm star-shaped poly(EO-*co*-EEGE) (5.0g) was dissolved in 50 mL anhydrous DMSO and THF (v/v=3/2), and then a THF DPMNa solution (2.4mL) was injected into the solution to form initiator system. Then the initiator solution was added into the reaction kettle, sequentially, EO monomer (5.0g, 0.11mol) was injected into polymerization reaction system. Under stirring condition, the polymerization reaction was carried out at 60$^{o}$C for 48 h. Then the polymerization reaction was stopped by adding of 1mL acidified methanol. After all the solvents were removed by distillation under reduced pressure, the crude copolymers were dissolved in 20 mL dichloromethane, and then precipitated in cold diethyl ether. The chain length of PEO can be well controlled by adjusting the molar ratio of EO to end hydroxyl groups of macroinitiator star-shaped copolymers poly (EO-*co*-EEGE) during the anionic polymerization process.

### End-Capping Reaction of Star-shaped Block Copolymers Poly (EO-*co*-EEGE)-*b*-PEO.

The end hydroxyl groups of multi-arm star-shaped block copolymers poly(EO-*co*-EEGE)-*b*-PEO were end-capped by the reaction between hydroxyl groups and benzenecarbonyl chloride as end-capping reagent. The typical end-capping reaction procedure was shown as follows: Purified multi-arm star-shaped block copolymers poly(EO-*co*-EEGE)-*b*-PEO (4.0 g) was added to 50 mL anhydrous $CH_2Cl_2$, and then 1mL triethylamine and benzenecarbonyl chloride (2.0g) were introduced into reaction system at room temperature under stirring condition. The end-capping reaction solution was stirred for 24h, and then then precipitated in cold diethyl ether. The product was purified twice by dissolution/precipitation with $CH_2Cl_2$/diethyl ether. The precipitate was separated and dried in vacuum at 50 °C.

### Preparation of Multi-Arm Star-Shaped Block Copolymers Poly(EO-*co*-Gly)-*b*-PEO by Hydrolysis of the Ethoxyethyl Groups of Poly(EO-*co*-EEGE) Arms.

The cleavage reaction of ethoxyethyl groups was carried out according to literature.[55] Multi-arm star-shaped block copolymers poly(EO-*co*-EEGE)-*b*-PEO (2.0g) was added into 20 mL concentrated hydrochloric acid. The reaction system solution was stirred at room temperature for 2 h. The pH of the reaction solution was adjusted to 3.0 by addition of potassium hydroxide aqueous solution (5.0 M). The product was extracted with $CH_2Cl_2$ (100mL×2), and then the organic layer was dried over anhydrous $MgSO_4$. 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 poly(EO-*co*-Gly)-*b*-PEO was obtained.

### Synthesis of Macroinitiator Multi-Arm Star-Shaped Block Copolymer Poly(EO-*co*-BiBGE)-*b*-PEO.

Multi-arm star-shaped block copolymers poly(EO-*co*-Gly)-*b*-PEO (1.0g) was dissolved in 50 mL of anhydrous NMP, then 5.2 mL of 2-bromoisobutyryl bromide was added dropwise at 0 °C for 30 min under vigorous stirring. The reaction system was stirred for 2 h at 0 °C, followed by stirring at room temperature for 24 h. After that, NMP solvent was removed by by distillation under reduced pressure. The residue was dissolved in $CH_2Cl_2$, and washed with NaOH aqueous solution (1 mol/L), HCl aqueous solution (1 mol/L), and DI water, respectively. After solvent was removed by distillation in vacuum, the final sample multi-arm star-shaped block copolymer poly(EO-*co*-2-bromoisobutyryloxyglycidyl ether)-*b*-PEO (poly(EO-*co*-BiBGE)-*b*-PEO) was dried in vacuum at 50°C for 5h.

### Preparation of Star-Shaped Brush-Like Block Copolymer (PEO-*g*-P*t*BA)-*b*-PEO by ATRP.

ATRP of *tert*-butyl acrylate (*t*BA) was performed using multi-arm star-shaped block copolymer poly(EO-*co*-BiBGE)-*b*-PEO as a macroinitiator possessing side initiation sites. In a typical polymerization process, an ampoule charged with CuBr (0.1415 g), PMDETA (0.3414 g), multi-arm star-shaped macroinitiator (0.2 g), *t*BA (46.8 mL), and 46 mL methyl ethyl ketone was degassed by three freeze-pump-thaw cycles in liquid nitrogen, then sealed and placed in an oil bath at 60 $^{o}$C. The ampoule was taken out from the oil bath and dipped in ice/water bath at different desired times to terminate the polymerization. The solution was then diluted with acetone and passed through a neutral alumina column to remove the catalyst, and precipitated in the mixture of methanol/water (v/v = 1/1). After filtration, the final product star-shaped brush-like block copolymer (PEO-*g*-P*t*BA)-*b*-PEO was purified by dissolution/precipitation twice with acetone and methanol/water, and dried at 60 °C in vacuum for 12h.

### Preparation of Water-Soluble Star-Shaped Brush-Like Block Copolymer (PEO-*g*-PAA)-*b*-PEO by Hydrolysis of the *tert*-Butyl Ester Groups on Side Chains.

In a typical process, star-shaped brush-like block copolymer (PEO-*g*-P*t*BA)-*b*-PEO (0.5 g) was dissolved in 50 mL $CH_2Cl_2$, and then 10 mL trifluoroacetic acid was added. The reaction solution was stirred at room temperature for 24 h. The resulting star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO was gradually precipitated in $CH_2Cl_2$ during the hydrolysis. The final sample was washed with $CH_2Cl_2$, and thoroughly dried under vacuum at 60 °C for 12h.

### Preparation of Multicompartment Polymeric Nanoreactors of Water-soluble Multi-Arm Star-Shaped Brush-Like Block Copolymers of (PEO-*g*-PAA)-*b*-PEO.

A 10 mg of multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO was dissolved in 10 mL anhydrous DMF, a good solvent for both PAA and PEO segments (c = 1 mg/mL) at room temperature. The resulting DMF solution was stirred for 2 days.

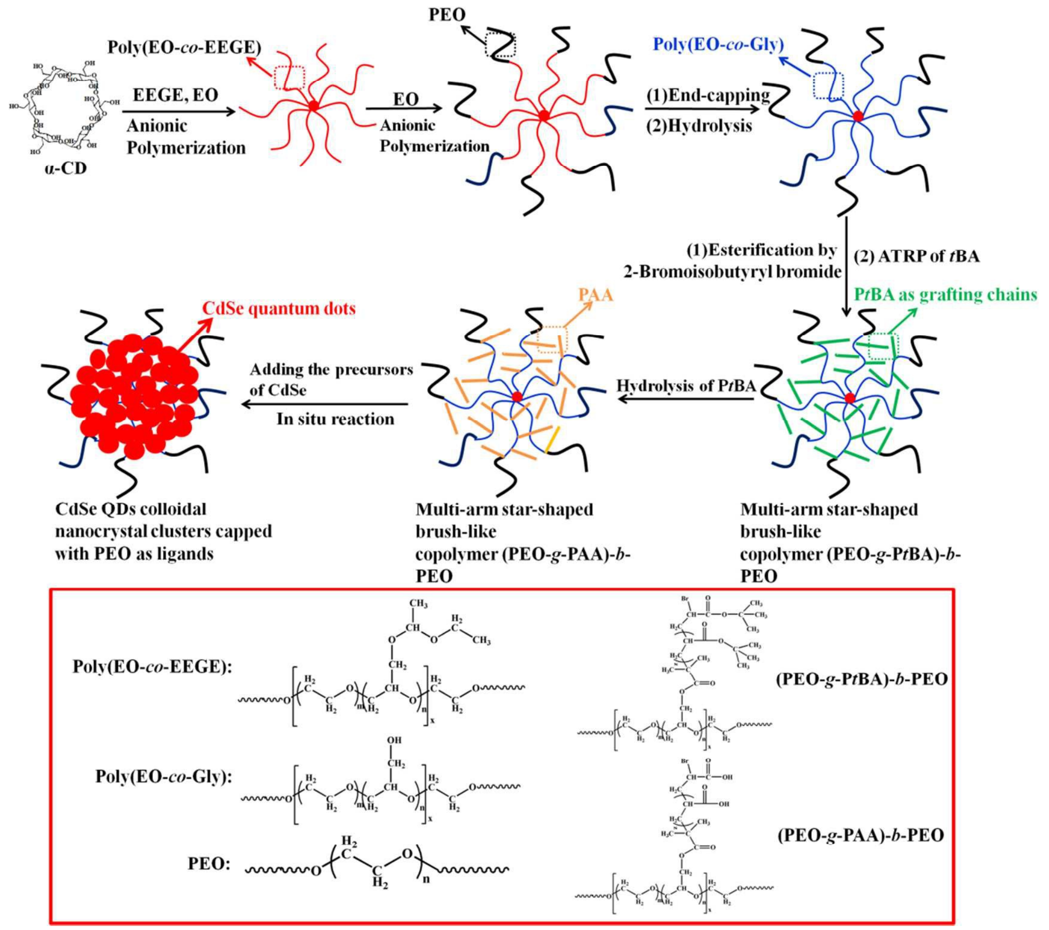
### Fabrication of Hybrid Inorganic-Organic Core-Shell CdSe QDs Colloidal Nanocrystal Clusters Capped with Hydrophilic PEO as Shell.

NaHSe was firstly prepared by reacting sodium borohydride and selenium powder in DI water. [56, 57] In a typical process, 1 mmol of selenium powder was introduced into 50 mL of DI water in a three-neck flask. After that, 3 mmol of $NaBH_4$ was added into reaction system under argon, and the reaction was carried out at room temperature for 8h under argon atmosphere. After that, the solvent was removed under vacuum, and NaHSe was re-dispersed in dry DMF to prepare DMF solution. After that, hybrid inorganic-organic core-Shell CdSe QDs colloidal nanocrystal clusters capped with hydrophilic PEO as shell were fabricated by the reaction of NaHSe and $Cd(acac)_2$. In a typical process, 10 mg star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO nanoreactors was dissolved in a 10 mL DMF at room temperature, followed by the addition of an appropriate amount of precursor $Cd(acac)_2$ that were selectively loaded into the inner PAA template compartment. The molar ratio of acrylic acid (AA) units in the PAA phase to precursors was 1:2. After that, an equimolar amount of freshly prepared NaHSe DMF solution was added dropwise at room temperature, the stirring was maintained for 1h under argon to ensure that all the precursors well dissolved in DMF solvent. The reaction system was then slowly heated to the boiling point of DMF and refluxed for 2h. The resulting CdSe colloidal nanocrystal clusters were washed by ethanol three time, and then dispersed into DI water.

## Results and Discussion

### Synthesis of Star-Shaped Brush-Like Block Copolymer (PEO-*g*-PAA)-*b*-PEO Template.

The procedure for preparation of star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO template was described in **Scheme 1**. Firstly, multi-arm star-shaped copolymers poly(EO-*co*-EEGE) 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. A multi-arm star-shaped copolymers poly(EO-*co*-EEGE) was formed. In the copolymerization system, DPMNa was utilized as deprotonating agent, which can easily react with hydroxyl groups to form alkoxides (i.e., anionic polymerization initiating sites). α-CD is a cyclic oligosaccharide consisting of six glucose units linked by α-1,4-glucosidic bonds.[58, 59] 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. A mixture of NMP and THF (v/v: 2/1) was used as solvent for copolymerization instead of THF for improving the solubility of α-CD and propagating alkoxides. In order to control anionic polymerization rate, only about 20% hydroxyl groups of α-CD were activated. In addition, owing to low solubility in organic solvent, if higher percentage of hydroxyl groups were deprotonated, alkoxides would precipitate from polymerization system. Under such conditions, all of the hydroxyl groups of α-CD could efficiently initiate the copolymerization of EO and EEGE because of the rapid exchange of protons between dormant hydroxyls and propagating alkoxides, and all the arms grew at the same rate.[60] Four multi-arm star-shaped copolymers poly(EO-*co*-EEGE) 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 monomers to initiator as **Table 1** (**Figure S1**).



**Scheme 1.** Schematic illustration of the synthesis of water-soluble multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO and as polymeric nanoreactors for the fabrication of CdSe quantum dot colloidal nanocrystal clusters capped with PEO as shell.

**Table 1.** Summary of multi-arm star-shaped copolymers poly(EO-*co*-EEGE)

| Sample | $R_f$[a] | Time (h) | $R_T$[b] | Conversion[c] (%) | $M_{n,\ GPC}$[d] (kg/mol) | PDI[e] | $M_{n,theory}$[f] (kg/mol) | $M_{n,arm}$[g] (kg/mol) | $N_{EEGE}$[h] |
|---|---|---|---|---|---|---|---|---|---|
| A-1 | 1/5 | 48 | 1/6.1 | 84.7 | 122 | 1.11 | 310 | 17 | 40 |
| A-2 | 1/5 | 48 | 1/6.6 | 89.6 | 192 | 1.08 | 630 | 35 | 77 |
| B-1 | 1/10 | 48 | 1/13.3 | 86.5 | 102 | 1.14 | 260 | 14 | 19 |
| B-2 | 1/10 | 48 | 1/13.6 | 87.3 | 168 | 1.06 | 560 | 31 | 42 |

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

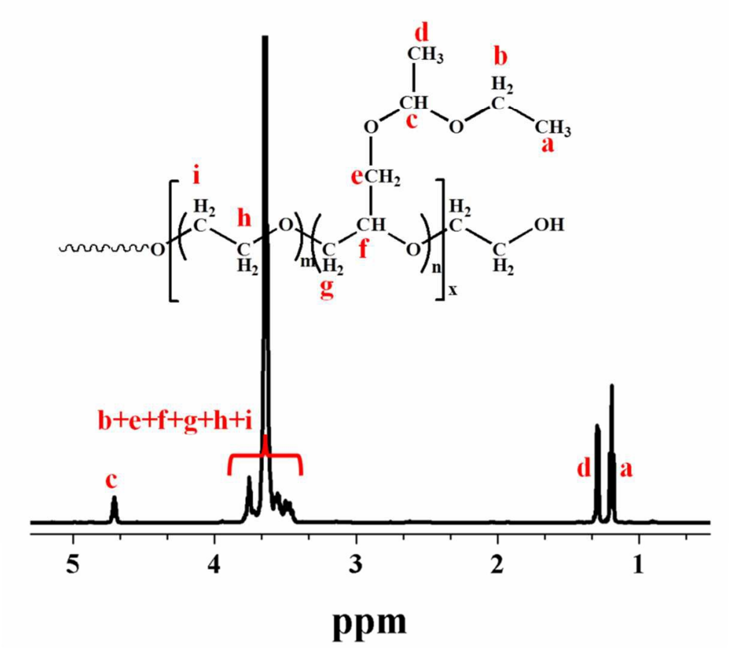


**Figure 1**. $^1$H-NMR spectum of multi-arm star-shaped copolymers poly(EO-*co*-EEGE) (A-1 sample was shown in **Table 1**, solvent: $CDCl_3$).

The **Figure 1** shows a typical $^1$H NMR spectrum of multi-arm star-shaped copolymers poly(EO-*co*-EEGE), 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:

$$R_T = \frac{4A_c}{A_{sum} - 7A_c} \qquad (2)$$

Where $R_T$ is the molar ratio of EEGE to EO in the resulting multi-arm star-shaped copolymers poly(EO-*co*-EEGE); $A_{sum}$ and $A_c$ represent the peak integral area sum of the protons (b+e+f+g+h+i) and the peak integral areas of the methine protons of the EEGE moiety, respectively. The $R_T$ values of four samples were shown in **Table 1**, 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 (3):

$$N_{EEGE} = \frac{M_{n,arm}}{(146 + \frac{44}{R_T})} \qquad (3)$$

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 1**.

Based the theory of copolymerization, the copolymer composition and the distribution of two monomers in resulting multi-arm star-shaped copolymers poly(EO-*co*-EEGE), are dependent on the monomer reactivity ratios. So, it is necessary to determine the monomer reactivity ratios. Reactivity ratio values of EO and EEGE may be evaluated by YBR method based on **Table 2** and **Figure 2**. [54] The monomer reactivity ratios for EO and EEGE: $r_{1(EO)}=1.18\pm0.03$ and $r_{2(EEGE)}=0.79\pm0.01$.

Due to $r_{1(EO)}>1$, $r_{2(EEGE)}<1$, and $r_1 \times r_2 \approx 1$, the theory of copolymerization leads the conclusion that the anionic copolymerization of EO and EEGE is apt to the ideal nonazeotropic copolymerization. During the copolymerization, the incorporation of two monomers into copolymer chains of star-shaped copolymer poly(EO-*co*-EEGE) is random, and EEGE units is randomly distributed along the copolymer chains.

**Table 2.** The Data summary of the Copolymerization of EO and EEGE.

| Sample | $R_f$[a] | Time (h) | $R_T$[b] | Conversion[c] (%) |
|---|---|---|---|---|
| 1 | 1/19 | 1 | 1/22.5 | 6.1 |
| 2 | 1/15 | 1 | 1/17.6 | 5.5 |
| 3 | 1/8 | 1 | 1/10.1 | 5.8 |
| 4 | 1/3 | 1 | 1/3.2 | 5.2 |
| 5 | 1/1 | 1 | 1/1.3 | 3.6 |
| 6 | 3/1 | 1 | 2.6/1 | 4.5 |

[a] The feed molar ratio of EEGE to EO. [b] The molar ratio of EEGE to EO in multi-arm star-shaped copolymer poly(EO-*co*-EEGE) calculated based on $^1$H NMR data. [c] Obtained by a gravimetric method.

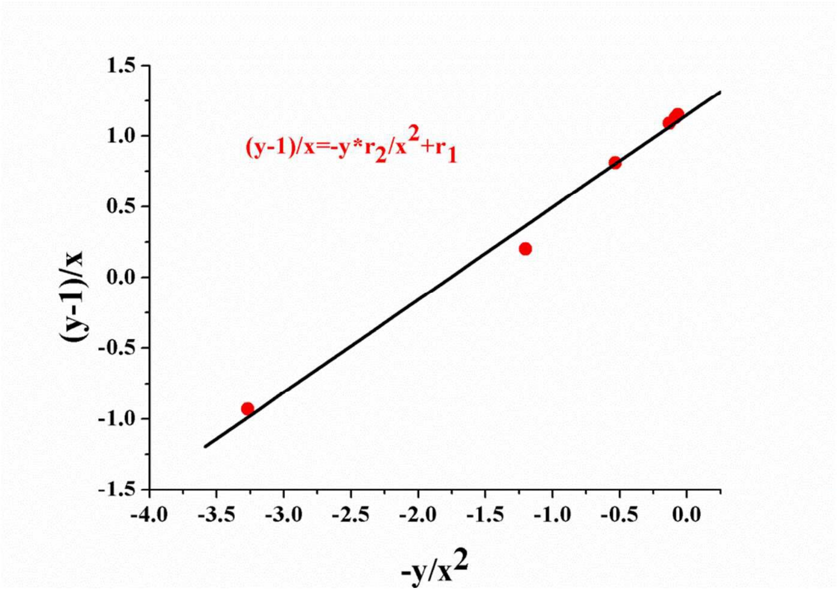


**Figure 2.** The dependence of (y-1)/x and –y/x$^2$ for the determination of monomer reactivity ratios during the anionic copolymerization of EO and EEGE, where $x$ is the feed molar ratio of EO to EEGE, $y$ is the molar ratio of EO to EEGE in the resulting copolymer. $r_1$ and $r_2$ are reactivity ratios of EO and EEGE, respectively.

In order to fabricate CdSe QD colloidal nanocrystal clusters capped with PEO as hydrophilic ligands using water-soluble multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO as polymeric nanoreactors, the second block hydrophilic homopolymer PEO chain growing on the first block poly(EO-*co*-EEGE) arm end is necessary. Sequential anionic polymerization strategy was used to polymerize monomer EO, the end hydroxyl groups of each arm of multi-arm star-shaped copolymers poly(EO-*co*-EEGE) and DPMNa exploited as macroinitiator system. The resulting multi-arm star-shaped block copolymers poly(EO-*co*-EEGE)-*b*-PEO samples were summarized in **Table 3**. After PEO chains growing from the end of poly(EO-*co*-EEGE) arm, obviously, molecular weight of each arm increased (**Figure S2**). 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 block copolymer poly(EO-*co*-EEGE)-*b*-PEO demonstrates the successful growing of the second block PEO (**Figure 3**).

**Table 3.** Summary of multi-arm star-shaped block copolymers poly(EO-*co*-EEGE)-*b*-PEO

| Sample | Time (h) | Conversion[a] (%) | $R_T$[b] | $M_{n,\ GPC}$[c] (kg/mol) | PDI[d] | $M_{n,arm}$[e] (kg/mol) |
|---|---|---|---|---|---|---|
| A-1a | 48 | 33.6 | 1/9.5 | 154 | 1.13 | 5.8 |
| A-2a | 48 | 35.9 | 1/8.4 | 235 | 1.11 | 5.2 |
| B-1a | 48 | 37.2 | 1/19.5 | 132 | 1.16 | 5.9 |
| B-2a | 48 | 36.7 | 1/16.3 | 206 | 1.10 | 6.2 |

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

In order to obtain multi-arm star-shaped brush-like copolymers (PEO-*g*-PAA)-*b*-PEO with well-defined structures, star-shaped brush-like PEO-*g*-PAA as core and PEO as shell, the end hydroxyl groups of multi-arm star-shaped block copolymers poly (EO-*co*-EEGE)-*b*-PEO must be deactivated by end-capping reaction. The end hydroxyl groups of multi-arm star-shaped block copolymers poly(EO-*co*-EEGE)-*b*-PEO were end-capped by the reaction between hydroxyl groups and benzenecarbonyl chloride as end-capping reagent. **Figure 3** shows the $^1$H-NMR spectrum after the end-capping reaction, the appearance of chemical shift at $\delta$ =6.89-7.24 ppm is assigned to the protons of phenyl groups as end group of arm chains. In addition, based on the he $^1$H-NMR spectrum after the end-capping reaction, the initiating efficiency of hydroxyl groups of α-CD at the first anionic polymerization can be evaluated by the following equation (4):

$$E_T = \frac{M_{n,arm}}{\dfrac{\dfrac{A_{sum}}{(4+3R_T)}}{\dfrac{A_P}{5}} \times (44+146R_T)} \times 100\% \qquad (4)$$

where $E_T$ is the initiating efficiency of hydroxyl groups of α-CD at the first anionic polymerization; $A_{sum}$ represents the integral area sum of the protons (b+e+f+g+h+i); $A_p$ represents the integral area of the protons of phenyl group as end-capping group; $R_T$ is the molar ratio of EEGE units to EO units in copolymers; 146 and 44 are the molar masses of EEGE and EO; $M_{n,arm}$ is the molecular weight of each block copolymer poly(EO-*co*-EEGE)-*b*-PEO arm calculated from the monomer conversion and the concentration of initiators. The $E_T$ value is nearly 100%, and this suggests that hydroxyl groups are almost completely growing into copolymer arms.

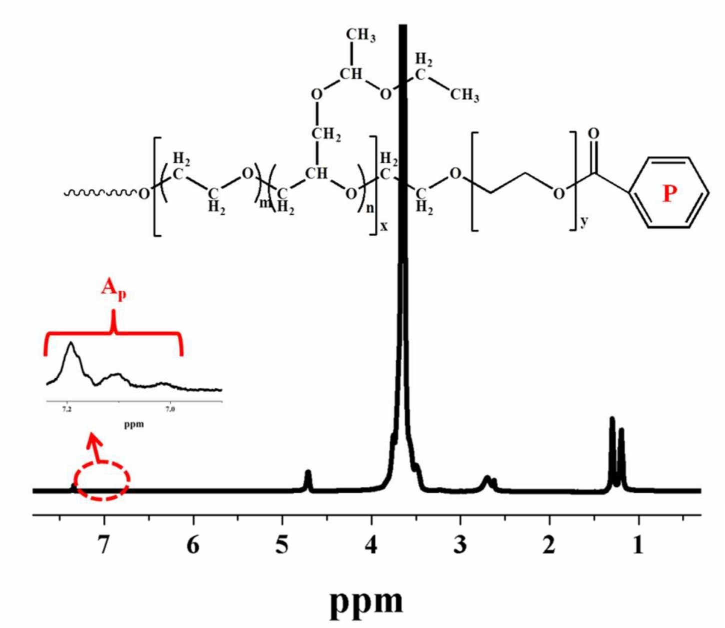


**Figure 3**. $^1$H-NMR spectrum of multi-arm star-shaped block copolymers poly(EO-*co*-EEGE)-*b*-PEO after the end-capping reaction by benzenecarbonyl chloride (A-1a sample was shown in **Table 3**, solvent: $CDCl_3$).

In **Scheme 1**, the procedure for the synthesis of multi-arm star-shaped brush-like copolymers (PEO-*g*-P*t*BA)-*b*-PEO was described. The ATRP of *t*BA monomer was carried out in methyl ethyl ketone at 60 °C, multi-arm star-shaped block copolymers poly(EO-*co*-BiBGE)-*b*-PEO as the macroinitiator (**Figure S5**, **Figure S6**), 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 (PEO-g-P*t*BA)-*b*-PEO 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 4**. **Figure 4** showed the $^1$H

NMR spectrum of the resultant multi-arm star-shaped brush-like block copolymers (PEO-g-P*t*BA)-*b*-PEO sample A-1b in **Table 4**. 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 (5):

$$M_{n,PtBA} = \frac{\frac{A_k}{9}}{\frac{A_j}{6}} \times 128.17 \qquad (5)$$

where $M_{n,PtBA}$ is the molecular weight of P*t*BA grafting side chains shown in **Table 4**, $A_k$ 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 4.** Summary of multi-arm star-shaped brush-like copolymers (PEO-*g*-P*t*BA)-*b*-PEO

| Sample | Time (h) | Conversion (%) | $M_{n,\ GPC}$[a] (kg/mol) | PDI[b] | $M_{n,PtBA}$[c] (kg/mol) |
|---|---|---|---|---|---|
| A-1b | 12 | 3.3 | 219 | 1.14 | 3.9 |
| A-2b | 12 | 4.5 | 322 | 1.13 | 4.6 |
| B-1b | 12 | 3.7 | 180 | 1.15 | 4.1 |
| B-2b | 12 | 4.1 | 270 | 1.09 | 4.5 |

[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.

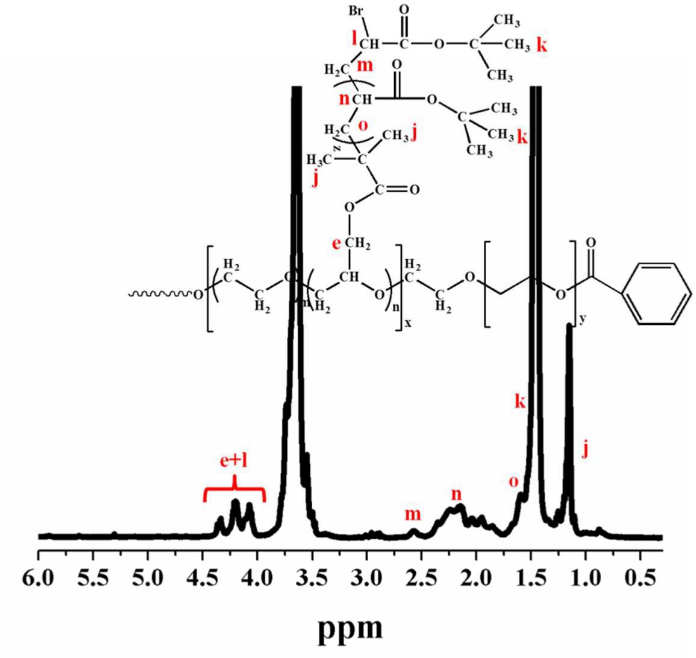


**Figure 4**. $^1$H-NMR spectrum of multi-arm star-shaped brush-like block copolymer (PEO-g-P*t*BA)-*b*-PEO (A-1b sample in **Table 4**, solvent: $CDCl_3$).

Finally, the water-soluble multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO 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 5**. 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 6**, 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$^{-1}$.

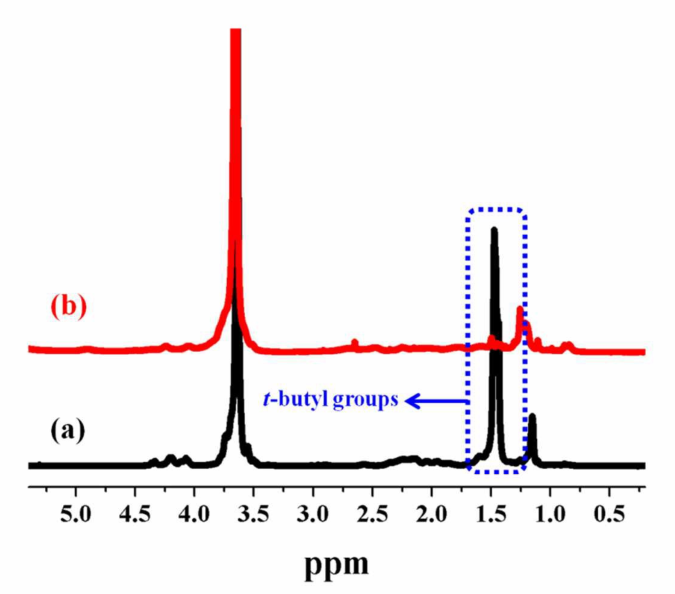


**Figure 5.** $^1$H NMR spectra of multi-arm star-shaped brush-like block copolymers (a) (PEO-*g*-P*t*BA)-*b*-PEO (Sample A-1b in **Table 4**) in $CDCl_3$ and (b) the resulting (PEO-*g*-PAA)-*b*-PEO in $CD_3OD$.

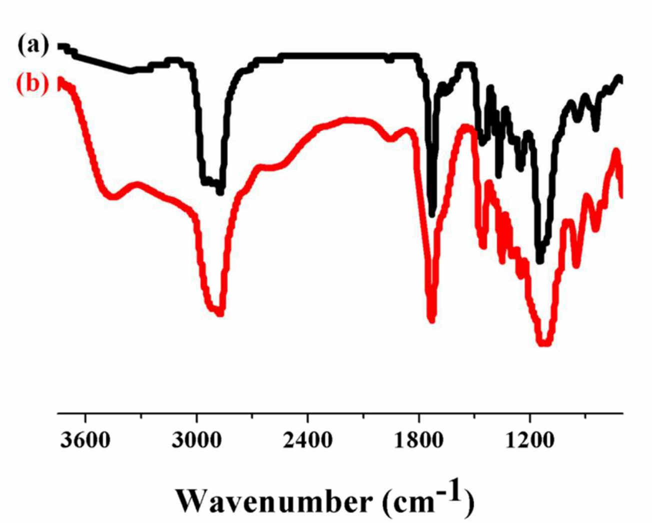


**Figure 6.** FT-IR spectra of multi-arm star-shaped brush-like block copolymers (a) (PEO-*g*-P*t*BA)-*b*-PEO (Sample A-1b in **Table S4**) and (b) the corresponding (PEO-*g*-PAA)-*b*-PEO.

## Fabrication of Hybrid Inorganic-Organic Core-Shell CdSe QD Colloidal Nanocrystal Clusters Capped with Hydrophilic PEO as Shell.

Quantum dots (QDs), as light-emitting particles on the nanometer scale, have emerged as a new class of materials for applications in solar cells,[61] LEDs,[62] tunable lasers,[63] biosensors,[64] bioimaging systems.[65] For QDs such as cadmium selenide (CdSe), variation of particle size provides continuous and predictable changes in optical absorption and fluorescence due to their quantum-confined nature. QDs synthesized via a conventional organometallic high temperature growth procedure are coated with hydrophobic ligands (e.g., trioctylphosphine oxide (TOPO)). However, on many occasions, it is desirable to prepare water soluble QDs for bioimaging, biosensor, QD-based devices, etc. [64, 65,66] In addition, as one of the most important manipulations for the applications, the assembling of these nanocrystals into the secondary nanostructures is highly desired in order to combine the properties of individual nanocrystals and their secondary structures due to interactions of the subunits.[67-69]

Owing to the ability of fabricating functional inorganic nanomaterials with well-defined structures, multimolecular micelles by aggregation of linear amphiphilic block copolymers were used as an attractive preparation strategy to fabricate functional colloidal nanocrystals via a combination with sol-gel processes.[43] Multimolecular micelles based on linear amphiphilic block copolymers, when their concentration is larger than the critical micelle concentration, are dynamically stable, and their morphology and structures in a given system depend heavily on temperature and solvent properties.[43, 70] With the changing of concentration, solvent properties, temperature, pH values, etc., the shapes and structures of multimolecular micelles may vary.[45] Comparing with multimolecular templates, the polymeric nanoreactors with uniform and structurally stable spherical structures from multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO are static rather than dynamic.[21, 71] After the water-soluble multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO was completely dissolved in polar solvent DMF, a good solvent for both PAA and PEO segments, polymeric nanoreactors were formed. AFM characterizations were performed to measure the characteristics of polymeric nanoreactors. Clearly, the water-soluble multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO formed spherical architectures with an average diameter of ~44 nm (**Figure 7**, **(a)** and **(b)**). In order to further investigate the architectures of star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO, TEM characterization was carried out. The dark spherical structures in the TEM micrographs corresponded to the hydrophilic PAA brush core as uranyl acetate preferentially stained the PAA segments of macromolecular architectures (**Figure 7**,

**(c)** and **(d)**). The average diameter of cores was 34±3.8 nm, and the size was smaller than that of AFM results owing to the second PEO as shell.

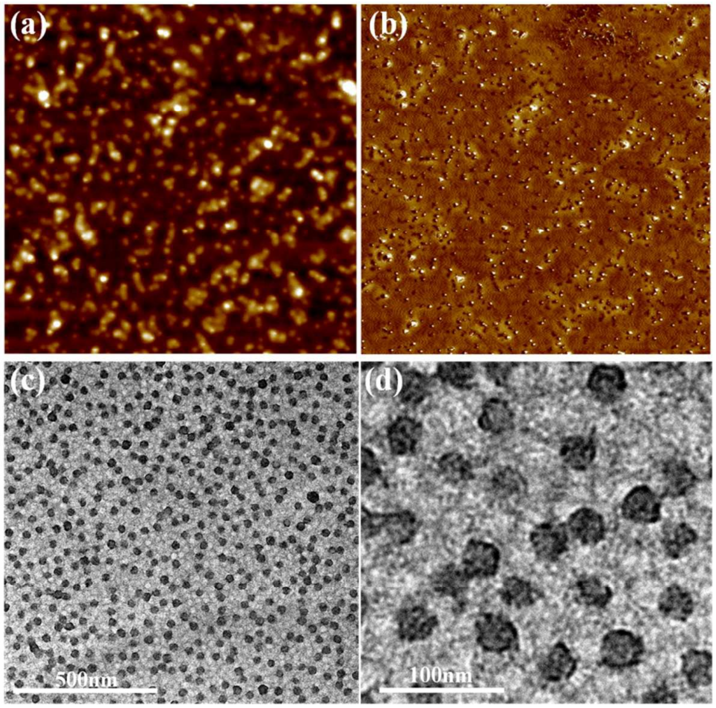


**Figure 7.** Morphology of the water-soluble multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO macromolecular structures. (a, b) AFM height and phase images of the water-soluble multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO (Sample A-1b as precursor in **Table 4**), respectively. image size= 5.0×5.0μm$^2$, Z range= 68nm for (a) and 27$^{o}$ for (b). (c, d) TEM images of the water-soluble multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO (Sample A-1b as precursor in **Table 4**) with different scale bars. The samples were treated with uranyl acetate before imaging to selectively stain the hydrophilic core PAA segments.

Subsequently, the water-soluble multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO was utilized as multicompartment polymeric nanoreactor to structure-direct the precursors of CdSe QDs into highly water-dispersed CdSe QD colloidal nanocrystal clusters. $Cd(acac)_2$ and NaHSe were used as precursors system, DMF as polar solvent. Precursors were loaded into PAA compartment of templates owing to the strong coordination of carboxyl groups with metal moiety of precursors. After that, hybrid inorganic-organic core-shell CdSe QD colloidal nanocrystal clusters were fabricated by the reaction of NaHSe and $Cd(acac)_2$, within which spherical CdSe colloidal nanocrystal clusters were intimately and permanently capped with hydrophilic PEO chains as shell on the surface to render the resulting clusters with highly water dispersible property. The morphology of spherical CdSe nanocrystal clusters with an average diameter of 29±3.3 nm was characterized by TEM, as demonstrated in the representative TEM images at different magnification in **Figure 8**. According to the close observation of these images, these uniform spherical colloids comprise small primary CdSe nanocrystals. The subunits of clusters can be investigated more clearly, and crystal lattices were clearly shown in **Figure 8(D)**, high resolution TEM (HR-TEM) image. Clearly, the spherical clusters consist of small primary nanocrystals as subunits with a diameter of 3.2±0.3 nm. X-ray diffraction (XRD) measurements also confirm the subunit crystal structure of CdSe colloidal nanocrystal clusters (**Figure S10)**. In addition, energy dispersive spectroscopy (EDS) microanalysis was also used to confirm the composition of CdSe QDs, as shown in **Figure S11**.

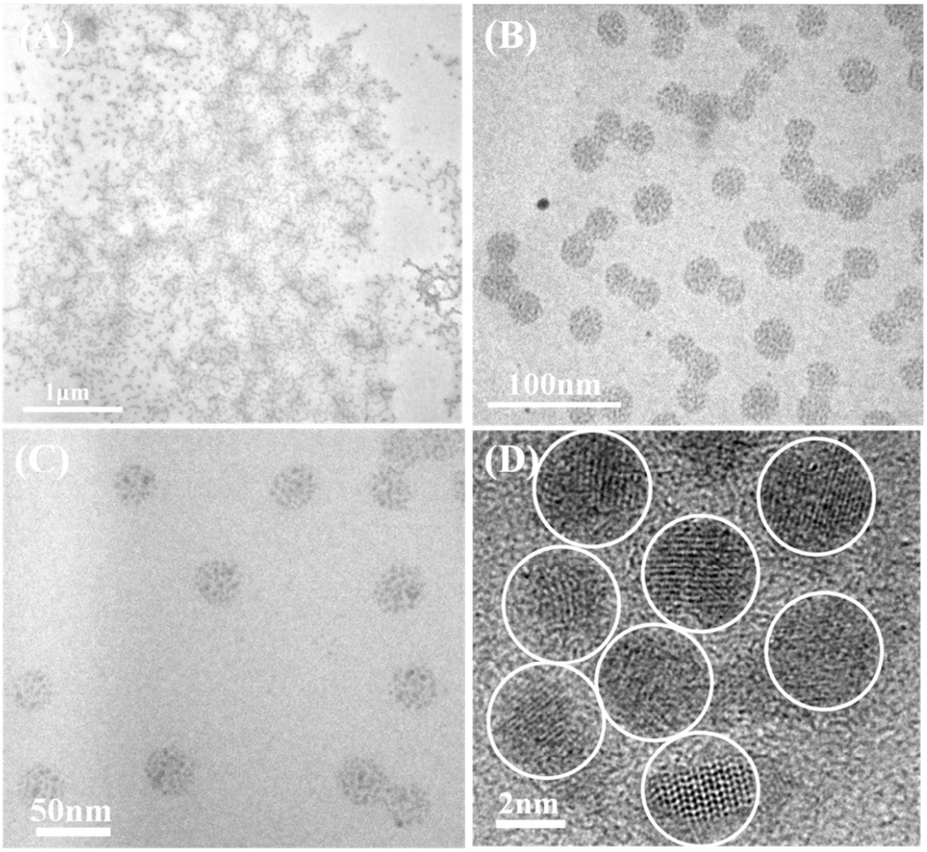


**Figure 8.** Representative TEM and HR-TEM images of CdSe colloidal nanocrystal clusters with different scale bars, the water-soluble multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO (Sample A-1b as precursor in **Table 4**) used as template. (a, b, c) Representative TEM images. (d) Typical HR-TEM image.

The UV-vis absorption and photoluminescence (PL) spectra of CdSe colloidal nanocrystal clusters coated with hydrophilic PEO polymer chains as shell dispersed in DI water shown in **Figure 9**. The absorption peak was at around 546 nm, and the emission peak was located at about 553 nm. Based on the absorption peak, the diameter of CdSe crystals as subunits in colloidal clusters can be calculated according to the previous reports in literature,[72, 73] $D \approx 2.9$ nm, which is correlated well with the TEM sizes of CdSe nanocrystals (see **Figure 8**). Owing to surface-tethered hydrophilic PEO polymer chains as shell, the resulting hybrid inorganic-organic core-shell CdSe colloidal nanocrystal clusters by star-shaped brush-like block copolymer polymeric nanoreactor are highly water-dispersed. Digital images of CdSe colloidal nanocrystal clusters dispersed into DI water were shown as insets in **Figure 9**. Notably, the aqueous solution of CdSe colloidal nanocrystal clusters emitted green fluorescence under UV illumination.

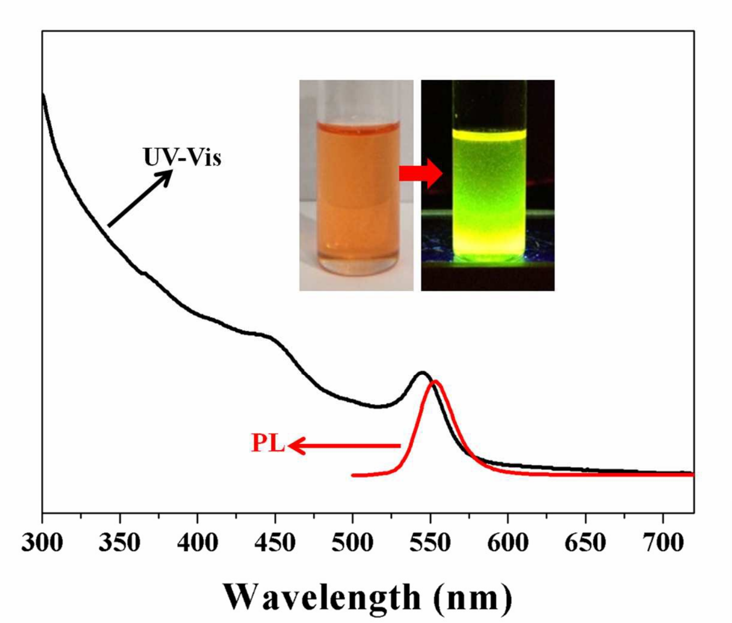


**Figure 9.** UV-vis absorption and photoluminescence (PL) spectra of CdSe colloidal nanocrystal clusters, the water-soluble multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO (Sample A-1b as precursor in **Table 4**) used as polymeric nanoreactor. The digital images of the aqueous solution of CdSe colloidal nanocrystal clusters before and after UV illumination are shown as insets.

## Conclusion

In summary, a series of novel water-soluble multi-arm star-shaped brush-like block copolymers, composed of hydrophilic PEO as main chain, hydrophilic polyelectrolyte PAA as functional graft chains, and the second PEO block as shell (i.e., multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO) with different molecular weights and grafting density, were rationally designed and synthesized by a combination of anionic copolymerization and ATRP. The anionic ring-opening copolymerization of EO and EEGE was conducted first by using α-CD with 18 hydroxyl groups and DPMNa as co-initiator system. The monomer reactivity ratios for EO and EEGE were also determined: $r_{1(EO)}=1.18\pm0.03$ and $r_{2(EEGE)}=0.79\pm0.01$, respectively. Then the resulting multi-arm star-shaped copolymers of poly(EO-*co*-EEGE) with hydroxyls as end functional groups were utilized as star-shaped macroinitiators to sequentially initiate the anionic ring-opening polymerization of monomer EO for the second block hydrophilic homopolymer PEO chain growing on the first block poly(EO-*co*-EEGE) arm end, and then ethoxyethyl groups of star-shaped block copolymers of poly(EO-*co*-EEGE)-*b*-PEO obtained were removed by hydrolysis. The forming multi-arm star-shaped block copolymers of EO and glycidol (Gly) with multi-pendant hydroxymethyls (star-shaped block copolymer poly(EO-*co*-Gly)-*b*-PEO) was then esterified by the reaction of pending hydroxyl groups of glycidol units of copolymers with 2-bromoisobutyryl bromide, and the resulting star-shaped brush-like macroinitiators were used to initiate the grafting copolymerization of *t*BA monomer by ATRP technique. Finally, the *tert*-butyl ester groups of P*t*BA grafting side chains were selectively hydrolyzed in trifluoroacetic acid to obtain the water-soluble multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO. The water-soluble star-shaped brush-like (PEO-*g*-PAA)-*b*-PEO, consisted of funcitonal PAA domain as core and hydrophilic PEO domain as shell, were exploited as polymeric nanoreactors to structure-direct in situ fabrication of CdSe QD colloidal nanocrystal clusters composed of primary CdSe nanocrystals as subunits. Spherical CdSe colloidal nanocrystal clusters were intimately and permanently capped with hydrophilic PEO chains on the surface to render the resulting clusters with highly water dispersible property. The present synthetic approach of functional copolymers with complicated structures is simple yet robust and may be extended to create a myriad of copolymers with different conformations and functions for fundamental study of the relationship between the architectures and their properties in solution and the solid state. Furthermore, going beyond the rational fabrication of CdSe colloidal nanocrystal clusters, we envision that, by judicious choice of different inorganic precursors, a family of intriguing functional colloidal nanocrystal clusters can be fabricated via the polymeric nanoreactor strategy.

## Acknowledgements

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## Supporting Information

GPC traces, $^1$H-NMR spectra, DLS characterization, TEM images of intermediates; XRD and EDS of CdSe colloidal nanocrystal clusters.

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# TOC Graphic

A series of novel water-soluble multi-arm star-shaped brush-like block copolymers, composed of hydrophilic PEO as main chain, hydrophilic polyelectrolyte PAA as functional graft chains, and the second PEO block as shell (i.e., multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO) with different molecular weights and grafting density, were rationally designed and synthesized by a combination of anionic copolymerization and ATRP, α-cyclodextrin as core. The water-soluble star-shaped brush-like (PEO-*g*-PAA)-*b*-PEO, consisted of funcitonal PAA domain as core and hydrophilic PEO domain as shell, were exploited as polymeric nanoreactors to structure-direct in situ fabrication of CdSe QD colloidal nanocrystal clusters composed of primary CdSe nanocrystals as subunits. Spherical CdSe colloidal nanocrystal clusters were intimately and permanently capped with hydrophilic PEO chains on the surface to render the resulting clusters with highly water dispersible property.