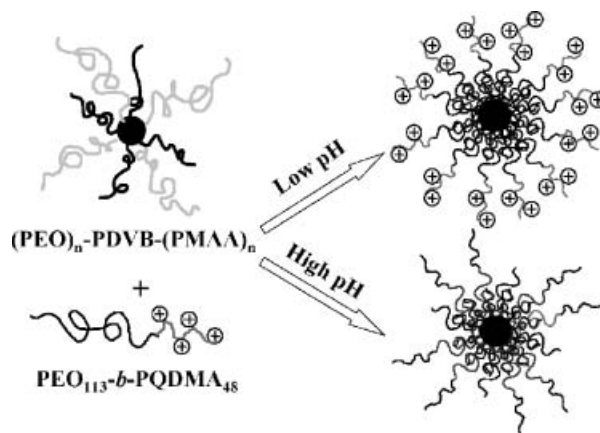


pH-Switchable Complexation between Double Hydrophilic Heteroarm Star Copolymers and a Cationic Block Polyelectrolyte

Zhishen Ge, Jian Xu, Danlu Wu, Ravin Narain, Shiyong Liu*

Double hydrophilic heteroarm star copolymers of poly(methacrylic acid) (PMAA) and poly(ethylene oxide) (PEO) were synthesized via atom-transfer radical polymerization (ATRP) using the “in-out” method. The synthesis consisted of three steps. Namely, ATRP was applied to the preparation of a star macroinitiator with PEO arms and a cross-linked core resulting from the polymerization of divinylbenzene (DVB) in the first step, chain extension with *tert*-butyl methacrylate (*t*BMA) under ATRP conditions, and subsequent hydrolysis of the *tert*-butyl groups afforded $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ heteroarm star copolymers with a cross-linked microgel core. This novel type of double hydrophilic heteroarm star copolymer can be considered as unimolecular micelles with hybrid coronas. The star copolymers exhibited pH-dependent solubility in water, being soluble at high pH and insoluble at low pH, due to the formation of hydrogen-bonded complexes between the PEO and PMAA arms. A mixed solution of the heteroarm star copolymer and a PEO-*b*-PQDMA diblock copolymer, where PQDMA is poly(2-(dimethylamino)ethyl methacrylate) fully quaternized with methyl iodide, remained stable in the whole pH range, and exhibited an intriguing pH-switchable complexation behavior accompanied with structural rearrangement.



Introduction

Star polymers typically consist of multiple linear polymer chains connected at one end to a focal junction point or a central microgel core.^[1,2] Due to their compact structure

and globular shape, they possess unique properties such as low melt and solution viscosity. Star polymers with hydrophilic arms and a hydrophobic microgel core can also be considered as unimolecular micelles.^[3–8] Compared to conventional block copolymer micelles, the long-term stability of unimolecular micelles argues well for their potential application as nanocarriers.^[9]

Star polymers can be prepared by three general approaches: growth from multifunctional initiators, attaching linear polymer chains to multifunctional linking agents, and employing difunctional monomers to build the core.^[1,2] Various synthetic techniques such as high-vacuum anionic polymerization,^[2,10,11] atom-transfer radical polymerization (ATRP),^[12–14] reversible addition-fragmentation chain transfer (RAFT),^[15–17] ring-opening

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polymerization (ROP),^[18–20] and nitroxide-mediated radical polymerization (NMP)^[21] have been successfully employed to prepare star polymers via the first approach. The second approach is usually employed in combination with anionic polymerization. It should be noted that the first two approaches typically lead to well-defined star polymers with a predetermined arm length and number of arms per star. For the third approach, terminally-reactive linear polymer chains are employed to initiate the polymerization of a difunctional monomer such as divinylbenzene (DVB). In most cases, when various “living” polymerization techniques are involved, the cross-linked microgel core of the formed star polymer is capable of initiating the same or a different type of monomer.^[11,22–29] Thus, although this approach usually leads to star polymers with less well-defined structures, they provides a facile “in-out” method for the preparation of heteroarm star polymers, such as (PS)_n-PDVB-(PCL)_m,^[23] (PS)_n-PDVB-(PI)_m,^[22,24] (PS)_n-PDVB-(P2VP)_m,^[25,26] (PS)_n-PDVB-(PBA)_m,^[27] and (PtBA)_n-PDVB-(PBA)_m,^[28] where PS, PEO, PCL, PI, P2VP, PBA, PtBA, and PDVB are polystyrene, poly(ethylene oxide), poly(ϵ -caprolactone), polyisoprene, poly(2-vinylpyridine), poly(*tert*-butyl acrylate), poly(*n*-butyl acrylate), and cross-linked poly(DVB) core, respectively.

All of the heteroarm star polymers listed above can be viewed as multiple hydrophobic, such as (PS)_n-PDVB-(PCL)_m,^[23] or amphiphilic diblock copolymer chains, such as (PS)_n-PDVB-(PEO)_m,^[30] linked together at the diblock junction point. In the past few years, increasing attention has been paid to linear and nonlinear-shaped double hydrophilic block copolymers (DHBCs).^[31–33] The constituting blocks of DHBCs are initially water soluble; however, the alteration of external conditions such as pH, temperature, or ionic strength can selectively render one block to be insoluble, leading to reversible or even structurally-invertible micellization behaviors. Therefore, the preparation of double hydrophilic heteroarm star polymers is highly desired.

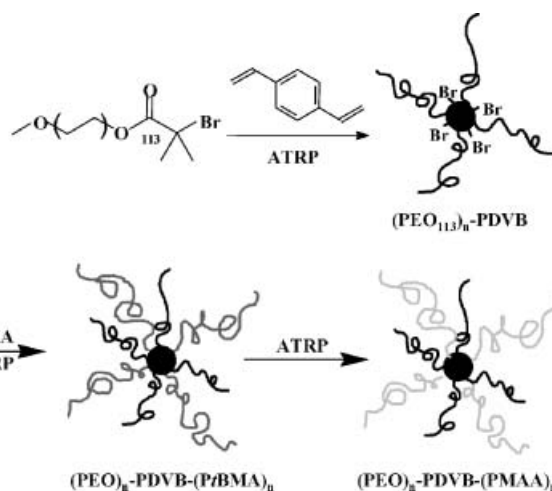
The driving force for the micellization of DHBCs is generally attributed to the microphase precipitation of the insoluble block and the affinity of the soluble block to the solvent; the phase separation of the insoluble block is arrested at early stages due to steric stabilization of the well-solvated block.^[34] Taking this perspective, the selective alteration of the solubility of one block, realized via polyelectrolyte complexation,^[35–41] hydrogen-bonded complexation,^[42–45] stereocomplexation,^[46] and metal-ion complexation^[47–50] have been successfully employed to fabricate colloidal nanoparticles, possessing micelle-like core-shell structures.

Stuart et al.^[51,52] recently reported the preparation of micelles with polyelectrolyte complexes as the core, stabilized by hybrid coronas. In the mixed solution of poly(2-

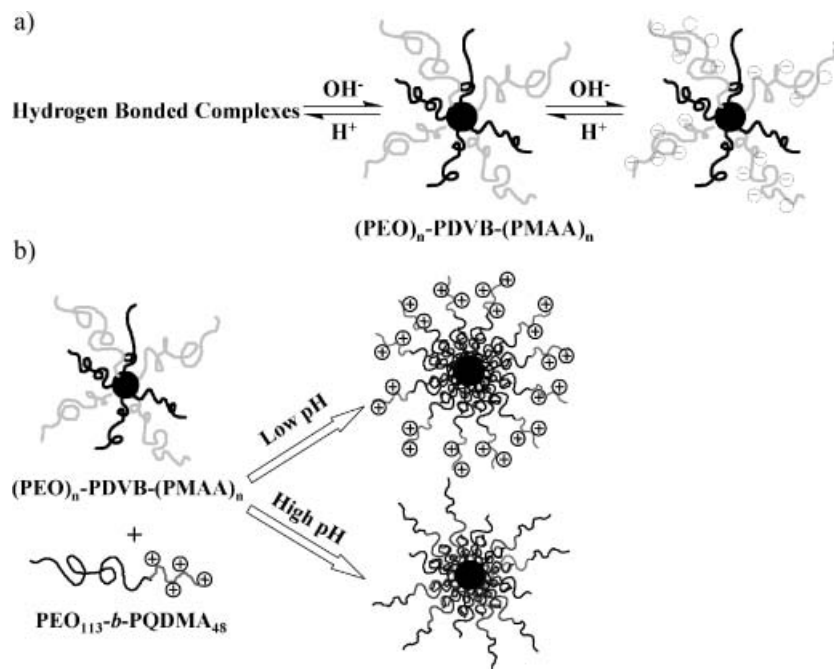
(dimethylamino)ethyl methacrylate)-*block*- poly(glyceryl methacrylate) (PDMA-*b*-PGMA) and poly(acrylic acid)-*block*-polyacrylamide (PAA-*b*-PAAm), the ionized PAA blocks and protonated PDMA blocks formed insoluble polyelectrolyte complexes costabilized by soluble PGMA and PAAm blocks. They further investigated the system by 2D ¹H NMR NOESY spectroscopy and concluded that the two types of corona chains mixed at the molecular level.^[53] In another system reported by the same group,^[54] double-faced micelles were formed due to segregation of the two types of corona chains. It should be noted that these two types of complex coacervate core micelles are structurally similar to heteroarm star copolymers with hydrophobic microgel cores.

On the other hand, Gohy et al.^[41] reported the pH-dependent micellization of a binary mixture of poly(ethylene oxide)-*block*-poly(2-vinylpyridine) (PEO-*b*-P2VP) and PEO-*b*-PMAA, where PMAA is poly(methacrylic acid). At high pH, PEO-*b*-PMAA remained molecularly dissolved, with PEO-*b*-P2VP forming P2VP-core micelles. At intermediate pH, colloidal particles formed with the core consisting of polyelectrolyte complexes between partially-ionized PMAA blocks and partially-protonated P2VP blocks, stabilized by soluble PEO blocks. At low pH, PEO blocks from both diblocks form insoluble hydrogen-bonded complexes with the PMAA block, stabilized in the corona by the protonated P2VP blocks. Armes et al.^[55] recently reported another example of pH-controlled formation of a “trinity” type of micelles.

Although heteroarm star copolymers with a cross-linked microgel core can be viewed as unimolecular micelles possessing hybrid coronas, they tend to further self-assemble into super-aggregates in selective solvents for one of the arms.^[25,29,56] Tsitsilianis et al.^[56] synthesized



Scheme 1. The synthetic route of (PEO)_n-PDVB-(PMAA)_m heteroarm star copolymers.



Scheme 2. (a) Possible modes of aggregate formation for $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ at different pH conditions in aqueous solution. (b) Schematic illustration of the pH-switchable complexation between the $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ heteroarm star copolymer and $\text{PEO}_{113}\text{-}b\text{-PQDMA}_{48}$ in aqueous solution.

$(\text{PS})_n\text{-PDVB-(P2VP)}_n$ heteroarm star copolymers via anionic polymerization. In toluene, a selective solvent for polystyrene (PS), the heteroarm star copolymer can self assemble into supermicelles; the aggregation number and core/corona dimensions strongly depended on the length of the insoluble and soluble arms. They also studied the stabilizing effect of PEO-*b*-P2VP on the superaggregates formed by $(\text{PS})_n\text{-PDVB-(P2VP)}_n$ in aqueous solution at different pH conditions.^[57]

In view of the above discussion, it is particularly interesting to investigate the supramolecular self-assembly behavior of stimuli-responsive double hydrophilic heteroarm star copolymers and their complexation with a linear diblock copolymer through pH-switchable electrostatic and hydrogen-bonding interactions. Herein, we report the first preparation of double hydrophilic heteroarm star copolymers via a combination of ATRP and the "in-out" method, the two types of polymer arms being PEO and PMAA, respectively (Scheme 1). $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ can be considered as unimolecular micelles with a hydrophobic PDVB microcore and hybrid coronas. Upon addition of PEO-*b*-PQDMA, where PQDMA is poly(2-(dimethylamino)ethyl methacrylate) fully quaternized with methyl iodide, the mixed solution remains colloidally stable in the whole pH range. ¹H NMR spectroscopy, transmission electron microscopy (TEM), laser light

scattering (LLS), and aqueous electrophoresis were used in combination to fully characterize the pH-switchable complexation behavior (Scheme 2).

Experimental Part

Materials

Monohydroxy-terminated poly(ethylene oxide) ($\text{PEO}_{113}\text{-OH}$; mean degree of polymerization (DP) = 113, $\overline{M}_n = 5000$, and $\overline{M}_w/\overline{M}_n = 1.07$) was purchased from Fluka and dried at 50 °C in vacuo overnight prior to use. Divinylbenzene (DVB, tech. 80%, Fluka), *tert*-butyl methacrylate (*t*BMA, Aldrich, 98%), and 2-(dimethylamino)ethyl methacrylate (DMA, Aldrich, 98%) were passed through silica columns and then vacuum distilled from CaH₂ and stored at -20 °C prior to use. *N,N,N',N'*-Pentamethyl-diethylenetriamine (PMDETA, TCI, 99%), CuCl, CuBr, 2,2'-bipyridine (bpy), (1-bromoethyl)benzene, and 2-bromoisobutyryl bromide were purchased from Aldrich and used without further purification. Triethylamine (TEA, 99%) and other chemicals were purchased from Shanghai Chemical Reagent Co. and purified according to standard procedures. The PEO-based ATRP macroinitiator ($\text{PEO}_{113}\text{-Br}$) was synthesized by esterification of the hydroxyl end groups of $\text{PEO}_{113}\text{-OH}$ using 2-bromoisobutyric acid in the presence of 1,3-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine as described in the literature^[58] with a yield of 97.8%.

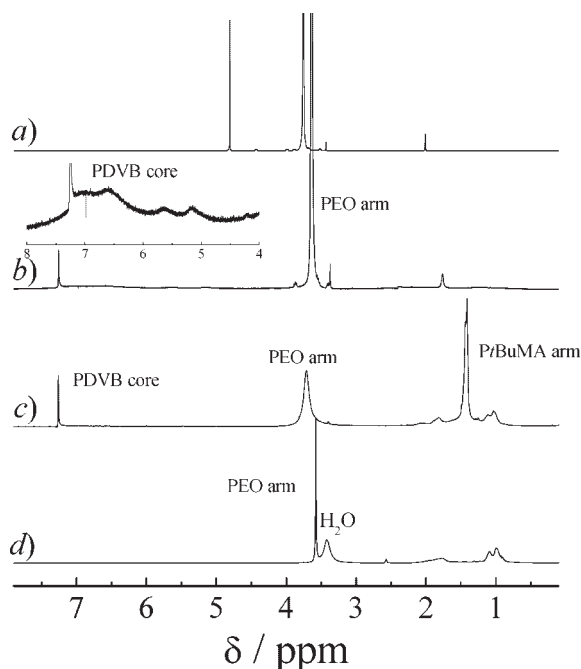


Figure 1. ^1H NMR spectra recorded for (a) $\text{PEO}_{113}\text{-Br}$ in D_2O , (b) $(\text{PEO})_n\text{-PDVB}$ star macroinitiator in CDCl_3 , (c) heteroarm star copolymer, $(\text{PEO})_n\text{-PDVB-(PtBMA)}_n$, in CDCl_3 , and (d) heteroarm star copolymer, $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$, in $\text{DMSO-}d_6$. The inset in Figure 1b showed the enlarged area in the range 4.0–8.0 ppm.

^1H NMR (CDCl_3 , ppm): $\delta = 2.0$ (6H, $\text{C}(\text{CH}_3)_2\text{-Br}$), 4.3 (2H, COOCH_2), 3.2–3.8 (450 H, $\text{OCH}_2\text{CH}_2\text{O}$). Figure 1(a) indicated that the degree of esterification of $\text{PEO}_{113}\text{-OH}$ was essentially 100%.

Synthesis

The general synthetic routes used for the preparation of the $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ double hydrophilic heteroarm star copolymer is shown in Scheme 1. The experimental details are described below.

Synthesis of the $(\text{PEO})_n\text{-PDVB}$ Star Macroinitiator

In a general procedure, a Schlenk flask equipped with a magnetic stirrer and a rubber septum was charged with CuBr (36 mg, 0.25 mmol), $\text{PEO}_{113}\text{-Br}$ macroinitiator (1.25 g, 0.25 mmol), DVB (0.89 mL, 0.65 g effective, 5.0 mmol), and anisole (3 mL). The flask was degassed by three freeze-pump-thaw cycles. Deoxygenated PMDETA (52 μL , 0.25 mmol) was injected and the reaction flask was then immersed in an oil bath thermostated at 100°C . After 7 h, the flask was quenched in liquid nitrogen. The crude product was dissolved in methylene chloride, passed through a column of basic alumina, and precipitated into diethyl ether. The obtained $(\text{PEO})_n\text{-PDVB}$ star macroinitiator was dried under vacuum at 40°C for two days.

Yield = 57.1% relative to DVB monomer.

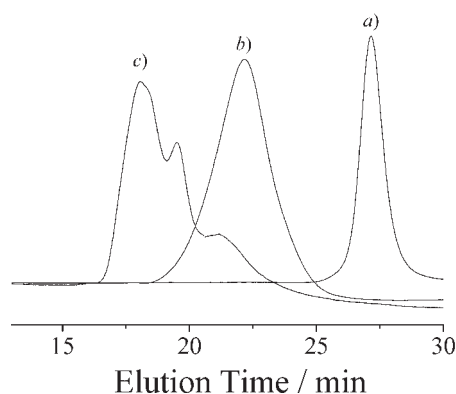


Figure 2. DMF GPC traces of a) $\text{PEO}_{113}\text{-Br}$ ($\overline{M}_n = 5200$, $\overline{M}_w/\overline{M}_n = 1.07$), b) $(\text{PEO})_n\text{-PDVB}$ star macroinitiator ($\overline{M}_n = 42300$, $\overline{M}_w/\overline{M}_n = 1.38$), and c) $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ heteroarm star polymer ($\overline{M}_n = 164700$, $\overline{M}_w/\overline{M}_n = 1.87$).

^1H NMR (CDCl_3): $\delta = 1.62$ (H_2O), 3.65 (PEO arms), 5.0–7.3 (PDVB core) ppm (Figure 1(b)).

GPC: $\overline{M}_n = 42300$, $\overline{M}_w/\overline{M}_n = 1.38$ (Figure 2(b)).

Synthesis of $(\text{PEO})_n\text{-PDVB-(PtBMA)}_n$ Heteroarm Star Copolymer

The heteroarm star copolymer was synthesized by ATRP using the $(\text{PEO})_n\text{-PDVB}$ star polymer as a macroinitiator. In calculating the feed ratios between the initiator and copper catalyst, we assume that there was no loss of Br functionality during the preparation of the $(\text{PEO})_n\text{-PDVB}$ star macroinitiator, and that all of the bromine end groups at the PDVB core remain accessible for the ATRP polymerization of $t\text{BMA}$ monomer. The molar content of Br end groups, n_{Br} was calculated by Equation (1):

$$n_{\text{Br}} = \frac{M_{\text{PEO}} \cdot \%_{\text{PEO}}}{5000} \quad (1)$$

where M_{PEO} and $\%_{\text{PEO}}$ are the mass and PEO weight fraction of the $(\text{PEO})_n\text{-PDVB}$ star macroinitiator.

A dry 25 mL Schlenk flask was charged with $(\text{PEO})_n\text{-PDVB}$ star macroinitiator (1.0 g, 0.15 mmol bromine end groups), CuCl (14 mg, 0.14 mmol), $t\text{BMA}$ (4.55 mL, 28 mmol), and anisole (6 mL). After the reaction mixture was frozen in liquid nitrogen, degassed PMDETA (29 μL , 0.14 mmol) was injected via degassed syringes. Three freeze-pump-thaw cycles were performed, and the flask was backfilled with nitrogen and brought back to room temperature to ensure a homogeneous dispersion. Polymerization was conducted in an oil bath at 70°C . At timed intervals, samples were withdrawn via a syringe fitted with stainless-steel needle for gas chromatography (GC) analysis to determine the monomer conversions. After 10 h, the reaction flask was quenched into liquid nitrogen. The reaction mixture was dissolved in methylene chloride, passed through a column of basic alumina, and then precipitated into a large amount of petroleum ether. The obtained $(\text{PEO})_n\text{-PDVB-(PtBMA)}_n$ was dried under vacuum at 30°C for 24 h, yielding 2.08 g of white powder.

^1H NMR (CDCl_3): $\delta = 0.9\text{--}2.1$ (PtBMA arms), 3.65 (PEO arms), 5.0–7.3 (PDVB core). (Figure 1(c))

GPC: $\bar{M}_n = 164\,700$, $\bar{M}_w/\bar{M}_n = 1.87$ (Figure 2(c)).

Hydrolysis of the Heteroarm Star Copolymer

$(\text{PEO})_n\text{-PDVB-(PtBMA)}_n$ was hydrolyzed into $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ double hydrophilic heteroarm star copolymer using HCl in refluxing tetrahydrofuran (THF) for 24 h. After hydrolysis, ^1H NMR spectroscopy signals corresponding to the *tert*-butyl groups in the PtBMA arms completely disappeared, indicating the successful transformation of $(\text{PEO})_n\text{-PDVB-(PtBMA)}_n$ into $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ (Figure 1(d), $\text{DMSO-}d_6$).

Synthesis of PEO-*b*-PQDMA

PEO-*b*-PDMA was synthesized via ATRP polymerization of DMA monomer in a 4:1 v/v 2-propanol/water mixture at 25 °C using $\text{PEO}_{113}\text{-Br}$ as macroinitiator and CuBr/bpy as catalysts.^[59] After 3 h, the monomer conversion was >98%. The reaction mixture was diluted with THF, passed through a column of basic alumina, and then precipitated into a large amount of petroleum ether. The degree of polymerization of the PDMA block in PEO-*b*-PDMA was determined to be 48 by ^1H NMR spectroscopy. GPC analysis revealed an \bar{M}_n of 12 800 and an \bar{M}_w/\bar{M}_n of 1.17. The obtained block copolymer was further quaternized with an excess of methyl iodide to form a neutral-ionic block copolymer, $\text{PEO}_{113}\text{-}b\text{-PQDMA}_{48}$.^[60]

Characterization

All of the ^1H NMR spectra were recorded using a Bruker 300 MHz spectrometer using D_2O or CDCl_3 as the solvent. The molecular weights and molecular-weight distributions were determined using a gel-permeation chromatography (GPC) line equipped with a Waters 1515 pump and a Waters 2414 differential refractive-index detector (set at 35 °C). It used a series of three linear Styragel columns - HT2, HT4, and HT5 - at an oven temperature of 50 °C. The eluent was *N,N*-dimethylformamide (DMF) at a flow rate of 1.0 $\text{mL} \cdot \text{min}^{-1}$. A series of low polydispersity polystyrene standards was employed for the calibration. Monomer conversions were determined from the concentration of the unreacted monomer in the samples, periodically removed from the reaction flask, using a Shimadzu GC-14B gas chromatography apparatus, equipped with a capillary column (DB-5, 30 m \times 0.25 mm \times 0.25 μm , J&W Scientific). Anisole was used as the internal standard for the calculation of the monomer conversions. Aqueous electrophoresis measurements were conducted at 20 °C using a Malvern Zetamaster S instrument. The solution pH was adjusted with concentrated NaOH and HCl.

A commercial spectrometer (ALV/DLS/SLS-5022F) equipped with a multi- τ digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He-Ne laser ($\lambda_0 = 632$ nm) as the light source was used for the dynamic and static LLS measurements. The specific refractive-index increment was determined using a precise differential refractometer at the same wavelength of 632 nm, as in the LLS measurements. For the determination of the absolute molar masses of the $(\text{PEO}_{113})_n\text{-PDVB}$ star macro-

initiator and the $(\text{PEO})_n\text{-PDVB-(PtBMA)}_n$ heteroarm star copolymer, Zimm plots were established over 14 angles in the range of 30–90 °. In dynamic LLS, scattered light was collected at a fixed angle of 90 ° for a duration of 15 min. The average hydrodynamic radius, $\langle R_h \rangle$, and the particle-size distributions were computed using CONTIN routines. All data were averaged over three measurements.

TEM observations were conducted on a Hitachi H-800 electron microscope at an acceleration voltage of 200 kV. The sample for TEM observations was prepared by placing a light drop of solution on a copper grid coated with thin films of Formvar and carbon successively.

Results and Discussion

In 1990, Tsitsilianis et al.^[61] established the “in-out” method by anionic polymerization for the first time. Then, Matyjaszewski^[62] extended this method to ATRP. Gnanou et al.^[12] reported the synthesis of double hydrophilic star block copolymers based on PEO and poly(acrylic acid) (PAA) by reacting PEO-*b*-PtBA macroinitiators with DVB under ATRP conditions. After hydrolysis, they successfully obtained star polymers with a PAA inner layer and PEO outer layer. Here, we aim to prepare double hydrophilic star polymers with hybrid PMAA and PEO arms. Starting from PEO-Br initiator, three steps are needed to synthesize $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ heteroarm star copolymers using ATRP via the “in-out” method (see Scheme 1). Firstly, DVB was employed to chain extend and cross-link the PEO-Br chains into the $(\text{PEO})_n\text{-PDVB}$ multifunctional star macroinitiator. Then, PtBMA chains were grown from the alkyl bromide initiating sites located at the core of the $(\text{PEO})_n\text{-PDVB}$ star polymer to produce $(\text{PEO})_n\text{-PDVB-(PtBMA)}_n$. Finally, hydrolysis of the PtBMA arms into PMAA produced the desired $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ double hydrophilic heteroarm star copolymer.

Synthesis of the $(\text{PEO})_n\text{-PDVB}$ Star Macroinitiator

Under standard ATRP conditions, reacting $\text{PEO}_{113}\text{-Br}$ with DVB will lead to chain extension and subsequent cross-linking of DVB, forming PEO star polymers with a cross-linked PDVB microgel core. The synthesis of $(\text{PEO})_n\text{-PDVB}$ star macroinitiator follows similar procedures to those employed by Chen et al.^[30] and Zhang et al.^[63] It is well known that DVB has a high affinity to radical addition and a relatively-low self-propagation rate. Thus, it favors star formation under standard ATRP conditions. The ^1H NMR spectrum of the $(\text{PEO})_n\text{-PDVB}$ star macroinitiator shown in Figure 1(b) confirmed the formation of a PDVB microgel core. Quite-broad peaks with low intensities from the aromatic and unpolymerized vinyl protons of the PDVB segments can be clearly observed (inset in Figure 1(b)). Due

to the highly cross-linked nature, the mobility of the PDVB microgel core is low and ^1H NMR spectroscopy cannot accurately report the molar ratio between the PEO arms and PDVB core.

Figure 2(a) and 2(b) show the DMF GPC traces of $\text{PEO}_{113}\text{-Br}$ and the $(\text{PEO})_n\text{-PDVB}$ star macroinitiator. $\text{PEO}_{113}\text{-Br}$ possessed a monomodal peak with low polydispersity, while the obtained $(\text{PEO})_n\text{-PDVB}$ star macroinitiator showed a relatively-broad monomodal peak, with a polydispersity index, $\overline{M}_w/\overline{M}_n$, of 1.38. A comparison between the two GPC traces led us to conclude that all the PEO macroinitiator participated in the polymerization of DVB and the formation of star polymers. We further found that when the amount of DVB is halved, GPC traces of the polymerization product revealed a small shoulder at the lower molecular weight side, possibly due to the formation of a small amount of PEO-*b*-PDVB linear chains without any cross-linking. Although the GPC analysis of the $(\text{PEO})_n\text{-PDVB}$ star macroinitiator gave an \overline{M}_n of 42 300, this value cannot be used to calculate the number of PEO arms per star polymer, due to the GPC elution time being only relevant to the hydrodynamic volumes of star polymers relative to those of PS standards. The microgel core and the branched conformation of the star polymer will severely lead to an underestimation of the molecular weight by GPC.

The absolute molar mass of the $(\text{PEO})_n\text{-PDVB}$ star polymer was determined in toluene to be $1.7 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$ by static LLS. The weight fraction of PEO in the star polymer can be estimated to be 77.1% from the monomer conversions of DVB (57.1%). Thus the number of PEO arms per $(\text{PEO})_n\text{-PDVB}$ star polymer was calculated to be ≈ 26 (i.e., $n = 26$).

Synthesis of $(\text{PEO})_n\text{-PDVB-(PtBMA)}_n$ and Subsequent Hydrolysis

The polymerization of *t*BMA using the $(\text{PEO})_n\text{-PDVB}$ star macroinitiator by ATRP can lead to the formation of $(\text{PEO})_n\text{-PDVB-(PtBMA)}_n$ heteroarm star copolymers. Although the reaction seems quite straightforward, major concerns arise due to the accurate initiation efficiency of the star macroinitiator.^[27,28] In earlier reports of the preparation of heteroarm star copolymers, the number of polymer chains of the second monomer per heteroarm star copolymer was simply considered to be equal to the number of alkyl bromine initiating sites at the PDVB microgel core.^[23,62] For simplicity, the initiation efficiency for the polymerization of *t*BMA in the current study was also assumed to be 100%.

Figure 1(c) shows the ^1H NMR spectrum of the $(\text{PEO})_n\text{-PDVB-(PtBMA)}_n$ heteroarm star copolymer, revealing the presence of signals from PEO and PtBMA arms. The

signals of the PDVB microgel core are almost negligible. On the basis of an integral ratio of peaks at $\delta = 3.6$ ppm characteristic of PEO, with that at $\delta = 1.3$ ppm characteristic of PtBMA, the degree of polymerization (DP) of each PtBMA arm is calculated to be ≈ 48 if we assume that all of the $(\text{PEO})_n\text{-PDVB}$ star macroinitiators have participated in the polymerization of the *t*BMA and the number of PtBMA arms is equal to that of PEO arms per heteroarm star copolymer.

Figure 2(c) shows the DMF GPC trace of $(\text{PEO})_n\text{-PDVB-(PtBMA)}_n$. A relatively-broad and multimodal elution curve can be observed, yielding an apparent \overline{M}_n of 164 700 and an $\overline{M}_w/\overline{M}_n$ of 1.87. The presence of a peak at the lower molecular weight side can be clearly ascribed to unreacted $(\text{PEO})_n\text{-PDVB}$ star macroinitiator. The other two main peaks may be ascribed to normal heteroarm star copolymer, the interstar coupling product, and/or star copolymer with different numbers of arms or arm lengths. Thus, the above calculation of the DP of PtBMA arms represents a quite rough estimation.

Recently, Matyjaszewski^[27,28] proposed a convenient method to determine the initiation efficiency of a PDVB-based star macroinitiator, by comparing the kinetic parameters obtained from ATRP polymerizations initiated by star macroinitiator and small molecule initiator. Assuming that the initiation efficiency of the small molecular initiator was 100%, they successfully obtained the initiation efficiency of the star macroinitiators. Theoretically, relatively-accurate initiation efficiency and number of PtBMA arms per $(\text{PEO})_n\text{-PDVB-(PtBMA)}_n$ heteroarm star polymer can be obtained following similar principles. We further transformed $(\text{PEO})_n\text{-PDVB-(PtBMA)}_n$ into $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ heteroarm star polymer via acid-catalyzed hydrolysis (Scheme 1). As discussed in the Experimental Part, ^1H NMR spectroscopy studies (Figure 1(d)) suggested 100% hydrolysis of the PtBMA arms into PMAA arms; we thus successfully obtained $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$.

pH-Tunable Aggregation Behavior of $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$

In aqueous solution, PEO and PMAA can form hydrogen-bonded complexes with 1:1 repeating molar units.^[64] The complexes can be broken by neutralization of the PMAA with NaOH. Gohy et al.^[41] and Tenhu et al.^[65–67] studied the self-complexation and micelle formation of PEO-*b*-PMAA when one of the blocks is much longer than the other.

$(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ heteroarm star copolymer cannot be directly dissolved in water. However, upon addition of concentrated NaOH, it can be dissolved and the solution is apparently clear in the concentration range $0.1\text{--}5 \text{ g} \cdot \text{L}^{-1}$.

The apparent molar mass of $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ in aqueous solution ($\text{pH} = 10$) was determined to be $3.7 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$ by static LLS. Theoretically, the molecular weight of $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ can be estimated to be $\approx 3.0 \times 10^5$ from the absolute molar mass of $(\text{PEO})_n\text{-PDVB}$ ($1.7 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$, static LLS) and the number/DP of PMAA arms in $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$. Thus, $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ star polymers are molecularly soluble in aqueous solution at $\text{pH} = 10$. Addition of HCl leads to macroscopic phase separation below $\text{pH} = 5.7$, and the dissolution/precipitation cycle is fully reversible upon pH alterations. This clearly indicates the aggregation between heteroarm star copolymers at low pH. It is well known that carboxylic-acid groups in PMAA have a pK_a of 5.5,^[68] thus hydrogen bonding interactions between PMAA and PEO arms should be responsible for the aggregation between unimolecular micelles (Scheme 2).

Above $\text{pH} = 7$, PMAA arms remained almost fully ionized and there was no possibility of hydrogen-bonding interactions between the PEO and PMAA. This should correspond to the molecular dissolved states. It should be noted that the PEO and PMAA arms were connected to a hydrophobic PDVB core; thus, the star polymer resembles unimolecular micelles with hybrid coronas.^[53,54] Procházka et al.^[69,70] also prepared hybrid polymeric micelles with hydrophobic PS cores and mixed shells of PEO and PMAA. This type of hybrid micelle was structurally similar to the heteroarm star copolymer studied in our case. Gorodyska et al.^[71] prepared star-shaped PS-P2VP block copolymer single molecules and studied them using AFM. In a selective solvent the unimers showed a core-shell structure with hydrophobic PS cores and mixed shells of PS and P2VP.

pH-Switchable Complexation between $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ and $\text{PEO}_{113}\text{-}b\text{-PQDMA}_{48}$

We further studied the stabilization effect of a neutral-cationic diblock copolymer, $\text{PEO}_{113}\text{-}b\text{-PQDMA}_{48}$, on the unimolecular micelles with hybrid coronas, $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$, at different pH conditions. Two types of non-covalent interactions need to be considered here: hydrogen-bonding interactions between the PEO and PMAA at low pH, and electrostatic interactions between the PQDMA and ionized PMAA at high pH. It was expected that these two types of interactions can be switched by adjusting the solution pH. Only PMAA chains

in their neutral form will interact with the PEO via hydrogen-bonding interactions; while for ionized PMAA, they will form polyelectrolyte complexes with PQDMA.^[55] A schematic illustration is shown in Scheme 2.

All of the carboxyl groups of the PMAA arms remain ionized at $\text{pH} = 10$. Thus, $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ can be viewed as unimolecular micelles with hybrid PEO and ionized PMAA arms. Upon mixing with $\text{PEO}_{113}\text{-}b\text{-PQDMA}_{48}$, the mixed solution with the weight fraction of $\text{PEO}_{113}\text{-}b\text{-PQDMA}_{48}$ being 0.6 was stable and exhibited a bluish tinge, characteristic of colloidal particles. Dynamic LLS revealed an average hydrodynamic radius, $\langle R_h \rangle$, of $\approx 52 \text{ nm}$. The R_h distribution of the mixed solution was monomodal and rather narrow, and the polydispersity (μ_2/Γ^2) was ≈ 0.08 .

The actual morphology of the micellar aggregates at $\text{pH} = 10$ was observed by TEM (Figure 3(a)) that clearly revealed the presence of spherical nanoparticles of around 40–60 nm in diameter. As TEM determined the micelle dimensions in the dry state, while dynamic LLS reports the intensity-average dimensions of micelles in solution which contains the contribution from the swollen corona, so it is reasonable that the micelle sizes determined by TEM were smaller than those by LLS.

At a $\text{PEO}_{113}\text{-}b\text{-PQDMA}_{48}$ weight fraction of 0.6, the ratio between the repeating units of the ionized PMAA and the PQDMA is $\approx 1:1$. Polyelectrolyte complexation between the ionized PMAA and the PQDMA will take place, leading to the formation of three-layer “onion-like” micelles, similar to those formed by linear ABC triblock copolymers.^[59] The “onion-like” micelles should possess compact PDVB cores,

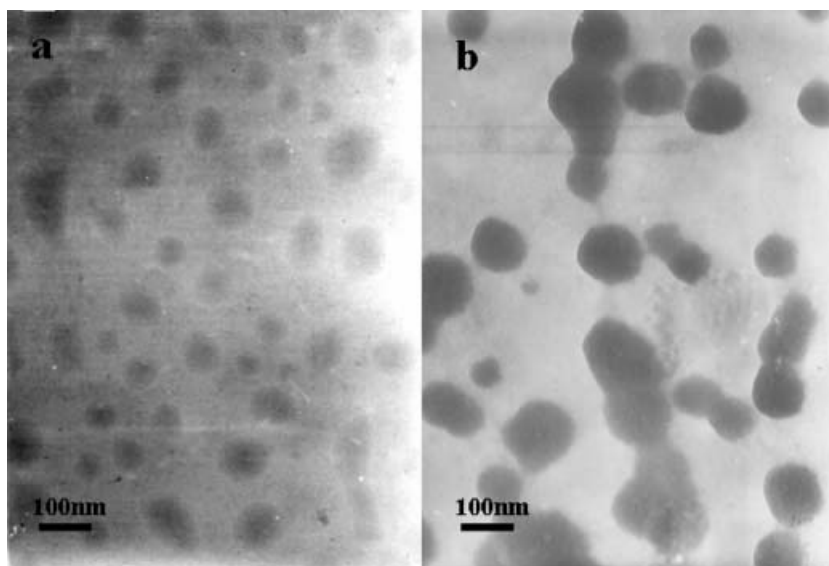


Figure 3. Typical TEM images of the mixed solution of $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ and $\text{PEO}_{113}\text{-}b\text{-PQDMA}_{48}$ in D_2O at (a) $\text{pH} = 10$ and (b) $\text{pH} = 3$; the weight fraction of the $\text{PEO}_{113}\text{-}b\text{-PQDMA}_{48}$ was 0.6.

an inner layer of polyelectrolyte complexes of the ionized PMAA and the PQDMA, and a protective PEO outer layer (Scheme 2).

^1H NMR spectroscopy studies were employed to confirm the above speculation (Figure 4). Compared to the spectra of $\text{PEO}_{113}\text{-}b\text{-PQDMA}_{48}$ and $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ (Figure 4(a) and 4(b)), the ^1H NMR spectrum of their solution mixture at $\text{pH}=10$ (Figure 4(c)) revealed the absence of signals of the backbone protons of the PMAA and the PDMA in the range 0.9–2.3 ppm. The signals characteristic of the PDMA block at $\delta=3.9$ and 3.3 ppm also disappeared and decreased to a large extent, respectively. Moreover, the signals characteristic of PEO were clearly evident. This confirmed that the complexation between PQDMA and ionized PMAA at $\text{pH}=10$ leads to decreased chain mobility of both blocks. The complexation will lead to the formation of a three-layer “onion-like” micellar structure as shown in Scheme 2.

Ionized PMAA arms will be gradually protonated upon decreasing the solution pH, and this will break up the electrostatic interactions between the ionized PMAA and the PQDMA. However, hydrogen-bonding interactions between the protonated PMAA and the PEO will occur. The PEO chains involved in this process may come from the heteroarm star copolymer and/or the diblock copolymer. If the latter is involved, the hydrogen-bonded complexes will

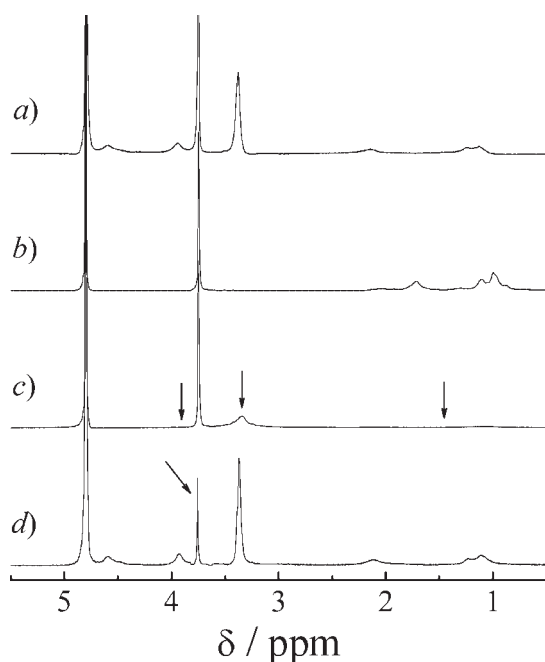


Figure 4. ^1H NMR spectra recorded for a) $\text{PEO}_{113}\text{-PQDMA}_{48}$ in D_2O , b) $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ in D_2O at $\text{pH}=10$, c) the mixed solution of $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ and $\text{PEO}_{113}\text{-}b\text{-PQDMA}_{48}$ in D_2O at $\text{pH}=10$, and d) the mixed solution of $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ and $\text{PEO}_{113}\text{-}b\text{-PQDMA}_{48}$ in D_2O at $\text{pH}=3$. The weight fraction of $\text{PEO}_{113}\text{-}b\text{-PQDMA}_{48}$ in the mixed solution was 0.6.

be stabilized by the PQDMA blocks (Scheme 2). This has indeed been proved to be the case. For the mixed solution of $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ and $\text{PEO}_{113}\text{-}b\text{-PQDMA}_{48}$ at a weight ratio of 2/3, the solution remained stable in the pH range 2–12. Apparently, the mixed solution was getting more bluish and scattering more light at $\text{pH}<6$, indicating that even larger aggregates were formed.

Figure 5 shows the variation of $\langle R_h \rangle$ with the solution pH for the mixed solution of $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ and $\text{PEO}_{113}\text{-}b\text{-PQDMA}_{48}$. Below $\text{pH}=6$, $\langle R_h \rangle$ shows a considerable increase to ≈ 90 nm at $\text{pH}=2$ from ≈ 50 nm at $\text{pH}>7$. The inflection point agreed quite well with the pK_a of PMAA.^[68] The TEM image shown in Figure 3(b) revealed the presence of spherical particles of $\approx 100\text{--}120$ nm in diameter at $\text{pH}=3$.

Compared to that of $\text{PEO}_{113}\text{-}b\text{-PQDMA}_{48}$ (Figure 4(a)), the ^1H NMR spectrum of the mixed solution at $\text{pH}=3$ (Figure 4(d)) revealed a considerable decrease of the signal intensities at 3.7 ppm, characteristic of PEO, relative to those at 3.3 ppm, characteristic of PQDMA. This strongly supported that at least some of the PEO segments in the diblock copolymer participated in the hydrogen bonding interactions with the neutral PMAA arms. At low pH, $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ exhibited macroscopic phase separation, which can be ascribed to the hydrogen-bonding interactions between the PEO and the PMAA arms. Thus, the stability of its mixed solution with $\text{PEO}_{113}\text{-}b\text{-PQDMA}_{48}$ should be ascribed to the stabilization effect of the PQDMA block. The formed colloidal particles again possessed an “onion-like” microstructure with a PDVB microgel core, an inner layer of the PEO/PMAA hydrogen bonded complexes, and the PQDMA outer corona.

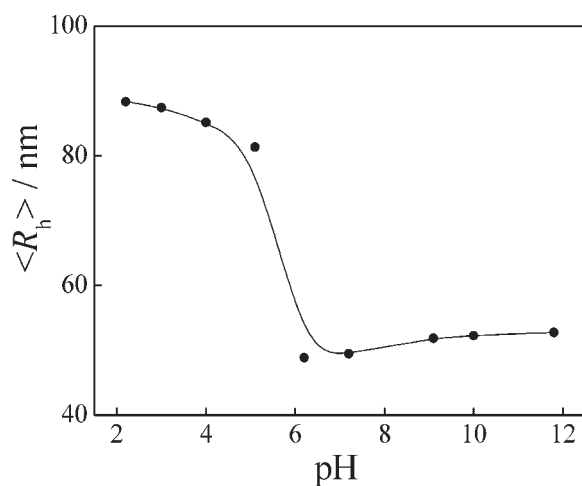


Figure 5. $\langle R_h \rangle$ as a function of solution pH for the mixed solution of $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ and $\text{PEO}_{113}\text{-}b\text{-PQDMA}_{48}$. The weight fraction of $\text{PEO}_{113}\text{-}b\text{-PQDMA}_{48}$ was 0.6 and the total polymer concentration was $0.5 \text{ g} \cdot \text{L}^{-1}$.

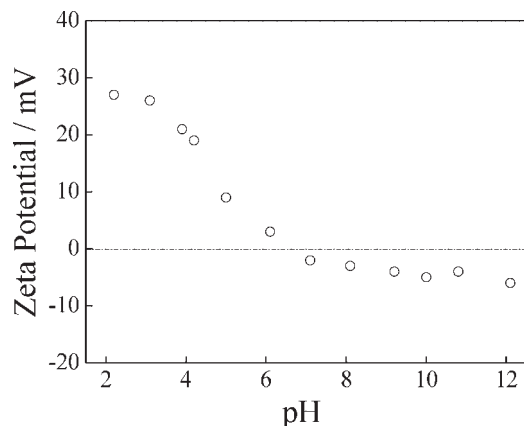


Figure 6. Zeta potential as a function of solution pH for the mixed solution of $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ and $\text{PEO}_{113}\text{-}b\text{-PQDMA}_{48}$. The weight fraction of $\text{PEO}_{113}\text{-}b\text{-PQDMA}_{48}$ was 0.6 and the total polymer concentration was $0.5 \text{ g} \cdot \text{L}^{-1}$.

The pH-switchable complexation between $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$ and $\text{PEO}_{113}\text{-}b\text{-PQDMA}_{48}$ in aqueous solution was further confirmed by aqueous electrophoresis (Figure 6). Above $\text{pH} = 7$, aqueous electrophoresis of the mixed solution revealed relatively-weak negative zeta potentials (-5 mV), indicating that the negative charges of the ionized PMAA arms are compensated by the positive charges in the PQDMA blocks through polyelectrolyte complexation. The “onion-like” micelles possessed neutral protective PEO coronas. Below $\text{pH} = 6$, the zeta potentials gradually increased to $+28 \text{ mV}$ at $\text{pH} = 2\text{--}3$. The hydrogen-bonded complexation between the neutral PMAA arms and the PEO took place; now the PQDMA blocks acted as stabilization coronas of the newly-formed colloidal particles (Scheme 2(b)). The measured isoelectric point was at $\text{pH} \approx 6$, which was close to the pK_a of the PMAA chains.

Conclusion

Double hydrophilic heteroarm star copolymers of poly(methacrylic acid) (PMAA) and poly(ethylene oxide) (PEO), $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$, where PDVB is a cross-linked microgel core of divinylbenzene (DVB), were synthesized via atom-transfer radical polymerization (ATRP) using the “in-out” method. The obtained heteroarm star copolymer exhibits pH-dependent solubility in water. However, upon addition of linear $\text{PEO-}b\text{-PQDMA}$ diblock copolymer, where PQDMA is poly(2-(dimethylamino)ethyl methacrylate) fully quaternized with methyl iodide, the solution mixture remains colloidally stable in the whole pH range. Based on the laser-light scattering (LLS), ^1H NMR spectroscopy, TEM, and aqueous electrophoresis results, we confirmed that at high pH, the PQDMA block and ionized PMAA arms

formed insoluble polyelectrolyte complexes, which were co-stabilized by PEO chains from both the $\text{PEO-}b\text{-PQDMA}$ and the $(\text{PEO})_n\text{-PDVB-(PMAA)}_n$. At low pH, the neutral PMAA arms and PEO formed hydrogen-bonded complexes, and the colloidal particles again possessed a hydrophobic PDVB core, an inner layer of PMAA/PEO hydrogen-bonded complexes, and a stabilizing PQDMA outer corona.

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