ARGET ATRP of Triblock Copolymers (PMMA-b-PEO-b-PMMA) and Their Microstructure in Aqueous Solution

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ABSTRACT: Triblock copolymers poly(methyl methacrylate)-b-poly(ethylene oxide)-b-poly(methyl methacrylate) (PMMA-b-PEO-b-PMMA) with designed molecular weight of PMMA and PEO blocks were synthesized via the activator regenerated by electron transfer (ARGET) atom transfer radical polymerization (ATRP) of MMA. The Br-terminated Br–PEO–Br with the molecular weights of 20k and 100k were used as macroinitiators. ARGET ATRP was performed with ppm level amount CuBr2 as the catalyst and ascorbic acid as the reducing agent to overcome the sensitivity to oxygen in a traditional ATRP. The molecular weight of the PMMA block was manipulated by changing the molar ratio of monomers to the Br–PEO–Br macroinitiators. The synthesis of PMMA-b-PEO-b-PMMA and its structure was confirmed by Fourier transform infrared and 1H NMR, and the molecular weight of the PMMA block was determined by 1H NMR. Aqueous solutions of PMMA-b-PEO-b-PMMA were prepared by solvent-exchange, and their microstructures were examined by tensiometry, static light scattering, and transmission electron microscopy. The effects of molecular weight of the PMMA and PEO blocks on the microstructure were elucidated.

INTRODUCTION

Associative polymers (APs) are polymers with blocky segments that have a tendency to associate in selective solvents.1 The APs can self-assemble to form different types of microstructures as a result of their association in selective solvents, yielding some very interesting properties. These systems have been exploited in many applications, including controlled drug release, rheology modifier, and polymer flooding for enhanced oil recovery.1-5 The APs are amphiphilic due to the presence of both hydrophilic and hydrophobic segments, resembling the structure of surfactants.6,7 The hydrophobic and hydrophilic segments self-associate to form a core–shell structure consisting of a hydrophobic core and a hydrophilic corona. Triblock copolymer APs with BAB structure have attracted increasing attention due to their unique structure and associative properties, where A is the hydrophilic block and B is the hydrophobic block.8-11 When both ends of the BAB triblock copolymers associate in dilute aqueous solution, they form a hydrophobic “B” core and a hydrophilic “A” corona with a flower-like micelle microstructure.5,11-13 The size and morphology of the flower micelle can be tuned at the molecular level by manipulating the chemical composition, architecture, and molecular weight.6

The control of the molecular weight of polymer is one of the critical issues in the polymer field, as it determines many properties of polymer materials, such as manufacturing process and mechanical properties. Many living radical polymerization methods have been developed to synthesize polymers with precise molecular weight and low dispersity, including nitroxide-mediated radical polymerization,14-16 organometallic mediated radical polymerization,17,18 reversible addition–fragmentation chain-transfer polymerization,19,20 and atom transfer radical polymerization (ATRP).21-25 In all these living radical polymerization processes, the reactive polymer chain ends are preserved by a reversible reaction between the active and dormant species, leading to a low and constant concentration of the radicals. The reversible reaction in ATRP is mediated by redox-active transition-metal complexes (i.e., CuI/ligand and CuII/ligand) as catalysts and alkyl halides as initiators.21,25 ATRP is one of the most popular living radical polymerization methods because it is easy to setup, efficient, robust, and tolerant to impurities and monomers types.25 It has been extensively used to synthesize polymers with well-
controlled molecular weights and architecture, such as block copolymer and star-like polymers.\textsuperscript{21,28−31}

However, the apparent drawbacks of the classical ATRP limit its applications in the industry, where a relatively large amount of catalyst, typically in the order of 0.1−1 mol % relative to monomer contents, are normally used to achieve a well-controlled living radical polymerization process.\textsuperscript{21} Thus, there is a significant amount of catalyst present in the final products, and the removal of metal complex is time-consuming and expensive. As the catalysts are generally toxic, the removal is necessary before using the final product. Sometimes, the residues of the catalyst are very difficult to remove, and this severely limits the application of ATRP.\textsuperscript{32} Moreover, the catalysts used in the classical ATRP are metal complexes at low valence states (i.e., CuBr), which is unstable under ambient conditions. Therefore, the catalyst for classical ATRP should be purified before use and then stored in a glovebox filled with inert gas. Another significant drawback of the classical ATRP is its sensitivity to oxygen, and tedious air-removing procedures are necessary, such as freeze−thaw cycling.\textsuperscript{21,52} Several modifications of ATRP have been developed to address the drawbacks of classical ATRP, such as simultaneous reverse and normal initiation ATRP,\textsuperscript{33−35} activators generated by electron transfer (AGET) ATRP,\textsuperscript{35,37} initiators for continuous activator regeneration ATRP,\textsuperscript{38} electrochemical ATRP,\textsuperscript{39,40} microwave-assisted ATRP,\textsuperscript{41−43} supplemental activator and reducing agents (SARA) ATRP,\textsuperscript{44−46} activator regenerated by electron transfer (ARGET) ATRP,\textsuperscript{21,22,24,47−50} and metal-free ATRP.\textsuperscript{32,47,48,51} In ARGET ATRP, metal complex at high valence states (i.e., CuBr\textsubscript{2}) are employed and excess reducing agents are added to steadily regenerate Cu(I) from Cu(II) as the catalyst. Compared to classical ATRP, ARGET ATRP requires a much lower concentration of Cu and is less sensitive to oxygen.\textsuperscript{21,24,52,53} Therefore, ARGET ATRP is a promising living radical polymerization method to synthesize polymers with controlled molecular weight and delicate designed architecture for industrial scale up.

Poly(ethylene oxide) (PEO) is a widely used hydrophilic polymer due to its significant water solubility and biocompatibility, and poly(methyl methacrylate) (PMMA) is a promising hydrophobic polymer due to its resistance to enzymatic attack, biocompatibility, appropriate glass transition temperature, and high transmittance.\textsuperscript{8,10,13} Amphiphilic block copolymers containing PEO as the hydrophilic blocks and PMMA as the hydrophobic blocks are of great interest due to their many potential applications.\textsuperscript{8,21,52,54,55} BAB triblock copolymers poly-(methyl methacrylate)-b-poly(ethylene oxide)-b-poly(methyl methacrylate) (PMMA-b-PEO-b-PMMA) with PEO and PMMA blocks of various molecular weights were used as model systems to study their association properties in aqueous solution. ATRP has been widely used to synthesize triblock copolymers;\textsuperscript{8,31,56−58} however, there is negligible report on the synthesis of PMMA-b-PEO-b-PMMA via ARGET ATRP. Here, ARGET ATRP was used to prepare PMMA-b-PEO-b-PMMA triblock copolymers with designed molecular weights. Br-initiating sites were first introduced to both ends of the
tyryl bromide (BIBB) was used to introduce Br-initiating sites to synthesize PMMA−b−PEO−Br macroinitiators for the ARGET ATRP of MMA to prepare BAB triblock copolymers. The Br−PEO−Br macroinitiators (P1 and P2) were synthesized via the esterification of PEO with BIBB in dichloromethane (DCM) in the presence of triethylamine (TEA) and deoxyadenosine monophosphate at room temperature. Excess BIBB was used in the esterification reaction of PEO to ensure that all the −OH groups of PEO were esterified to −C(CH3)2Br. The successful esterification of PEO by BIBB was confirmed by the Fourier transform infrared (FTIR) spectra of P1 and P2. As shown in Figure 1A, P1 and P2 showed typical bands of PEO at 2882 cm−1 (CH stretching), 1699 cm−1 (CH asymmetric stretching), 1466 cm−1 (CH2 scissoring), 1097 cm−1 (C−O−C stretching), 961 cm−1 (CH2 twisting), and 841 cm−1 (CH2 wagging). Moreover, the presence of the band at 1738 cm−1 in the FTIR spectra of P1 and P2 was attributed to the stretching vibration of C=O, indicating the successful esterification of PEO by BIBB.59 The structure of P1 and P2 was also studied by 1H NMR. As shown in Figure 1B, the peak in the 1H NMR at 3.6 ppm was assigned to the −O−CH2 of PEO. Compared to PEO, the P1 and P2 displayed a new peak at 1.9 ppm, which was assigned to the −CH2 of the −C(CH3)2Br moieties, suggesting the successful synthesis of P1 and P2.8,60

The BAB triblock copolymer PMMA−b−PEO−b−PMMA was synthesized via ARGET ATRP using Br−PEO−Br as the macroinitiator (Scheme 1). The ARGET ATRP of MMA was conducted with a small amount of CuBr2 as the catalyst and excess amount of ascorbic acid as the reducing agent. The molar ratio of CuBr2 to monomer is in the range of 50−250 ppm for the synthesis of PMMA−b−PEO−b−PMMA, and the purification of CuBr2 before use was not necessary. Compared to traditional ATRP, the ARGET ATRP reaction significantly reduced the amount of catalyst to ppm level. Because of the introduction of excess ascorbic acid as the reducing agent (50 times the catalyst), the ARGET ATRP was more tolerant to the presence of oxygen, and N2 purging was sufficient to remove air. The molecular weight of PMMA block was tuned by the molar ratio of MMA to the macroinitiator. Table 1 summarizes the molar ratio of MMA to the macroinitiator in the synthesis route of PMMA−b−PEO−b−PMMA and the obtained MMAs.

### RESULTS AND DISCUSSION

#### Synthesis and Mₘ of PMMA−b−PEO−b−PMMA.

The commercially available PEO possesses hydroxyl terminal groups at both ends. Scheme 1 shows the representative synthesis route of PMMA−b−PEO−b−PMMA. α-Bromoisobutyryl bromide (BIBB) was used to introduce Br-initiating sites on both ends of PEO. Then, the Br−PEO−Br was employed as the macroinitiator for the ARGET ATRP of MMA to synthesize PMMA−b−PEO−b−PMMA. The PEO with Mₘ of 20k or 100k was used as the hydrophilic A block in the BAB triblock copolymers. The Br−PEO−Br macroinitiators (P1 and P2) were synthesized via the esterification of PEO with BIBB in dichloromethane (DCM) in the presence of triethylamine (TEA) and deoxyadenosine monophosphate at room temperature. Excess BIBB was used in the esterification reaction of PEO to ensure that all the −OH groups of PEO were esterified to −C(CH3)2Br. The successful esterification of

![Figure 2](image_url)

Figure 2. (A) FTIR spectra of P1, P3, P4, and P5. (B) FTIR spectra of P2, P6, P7, and P8.
the ARGET ATRP and the targeted molecular weight. For the synthesis of P3, P4, and P5, the molar ratio of MMA monomer to P1 in the ARGET ATRP process were 100, 200, and 400, respectively. Therefore, the targeted molecular weight of PMMA were 5k for P3, 10k for P4, and 20k for P5. For the synthesis of P6, P7, and P8, the molar ratios of MMA monomer to P2 in the ARGET ATRP process were 400, 1000, and 2000, respectively. Thus, the target molecular weight of PMMA were 20k for P6, 50k for P7, and 100k for P8.

The successful implementation of the ARGET ATRP was confirmed by the synthesis of the final products, PMMA-b-PEO-b-PMMA. Figure 2 shows the FTIR spectra of the macroinitiators and PMMA-b-PEO-b-PMMA copolymers. Compared to P1, the FTIR spectra of P3, P4, and P5 displayed additional bands at 1728 and 750 cm\(^{-1}\), which were associated with the C=O and methyl vibration of the PMMA blocks. Moreover, the intensity of these two peaks increased with increasing \(M_n\) of the PMMA blocks. Similar phenomena were also observed for the FTIR spectra of P2, P6, P7, and P8 (Figure 2B). The results confirmed the successful synthesis of the triblock copolymers via ARGET ATRP and the \(M_n\) of the PMMA blocks increased with the feeding molar ratio of the MMA monomers to macroinitiator Br-PEO-Br.

To calculate the molecular weight of the PMMA block, the structure of PMMA-b-PEO-b-PMMA was examined by \(^1\)H NMR, as shown in Figure 3. Comparing the \(^1\)H NMR of P1 to that of P3, P4, and P5 revealed additional peaks at 3.6, 1.8, 1.0, and 0.8 ppm, which were attributed to \(-\text{O-CH}_3\) (e), \(-\text{CH}_2\) (c), and \(-\text{CH}_3\) (d) of the PMMA blocks.\(^{31}\) The intensity of these peaks increased with increasing \(M_n\) of the PMMA blocks. According to the integral area of PMMA to the PEO in the \(^1\)H NMR spectra and the \(M_n\) of PEO, the \(M_n\) of the PMMA was calculated using the following equation

\[
M_n \text{ of MMA} = \frac{(I_e + I_c + I_d) \times 4 \times M_n(\text{PEO})}{I_{a+b} \times 2 \times 8 \times 44} \text{ (g/mol)}
\]

where \(I_e\), \(I_c\), and \(I_d\) are the integrals of the corresponding e, c, and d protons of the PMMA blocks, \(I_{a+b}\) is the integral of the a and b protons of PEO, and 44 and \(M_n(\text{PEO})\) is the molecular weight of the repeating units of PEO and PEO, respectively. The monomer conversion of MMA in the ARGET ATRP could be deduced based on the calculated \(M_n\) and the target \(M_n\) of PMMA block using the following equation

\[
\text{monomer conversion} = \frac{\text{calculated } M_n \text{ of PMMA}}{\text{target } M_n \text{ of PMMA}}
\]

The calculated \(M_n\) of PMMA and corresponding monomer conversion are summarized in Table 1. The \(M_n\) of PMMA in P3, P4, and P5 was 3.7k, 7.8k, and 11.1k, respectively. The monomer conversion for the polymerization of P3 and P4 was reasonably high (74.0 and 78.0%, respectively), and the monomer conversion of P5 was moderate (55.5%). Similar \(^1\)H NMR spectra were obtained for P2, P6, P7, and P8. The \(M_n\) of PMMA blocks in P6, P7, and P8 determined from the \(^1\)H NMR spectra were 7.9k, 19.3k, and 32.2k, respectively. For the ARGET ATRP from P2, a medium monomer conversion (30–40%) was obtained for all the three polymers.

**Associative Microstructures of PMMA-b-PEO-b-PMMA in Aqueous Solutions.** The triblock copolymer PMMA-b-PEO-b-PMMA cannot be directly dissolved in water due to the long hydrophobic and high glass transition temperature of the PMMA block. The aqueous solutions of triblock copolymer were prepared by first dissolving the triblock copolymer in tetrahydrofuran (THF), followed by the slow addition of water at a rate of one drop every 10 s under vigorous stirring. After removing the THF via rotary evaporation, the aqueous triblock copolymer solutions were
obtained. Figure 4 shows the optical images of triblock copolymer aqueous solutions at a concentration of 0.1 wt%. For P3, P4, P5, and P6, the triblock copolymer aqueous solutions were transparent. However, the aqueous solutions of P7 and P8 were turbid, and precipitation was observed after 24 h due to the high amount of physical cross-linking formed in P7 and P8 aqueous solution.

The surface tension of the triblock copolymer aqueous solution was also studied as a function of concentration from 0 to 0.25 g/L. As shown in Figure 4C, the surface tension of all the triblock copolymer aqueous solutions decreased dramatically with concentration in the very dilute range of 0–0.003 g/L. The surface tension of the solution decreased from 72 to about 63 N/m at the concentration of 0.003 g/L. However, when the concentration was greater than 0.003 g/L, the surface tension decreased slowly with polymer concentration. The surface tension of PMMA-b-PEO-b-PMMA aqueous solution indicated that the critical micelle concentration (CMC) of these six triblock copolymers was about 0.003 g/L, and the CMC value was consistent with the CMC of PMMA-b-PEO-PMMA determined by fluorescence spectroscopy using pyrene as the probe. At the concentration above 0.1 g/L, the copolymer P3, P4, and P5 exhibited a lower surface tension than P6, P7, and P8 (Figure 5). Among them, P4 displayed the lowest surface tension of about 50 N/m at the concentration of 0.25 g/L (Figure 5).

The translation diffusion coefficient ($D_T$) and the hydrodynamic radius ($R_h$) of supernatant of the triblock copolymer aqueous solution were determined by dynamic light scattering. The intensity as a function of log $r$ at various scattering angles of these six triblock copolymer solutions is shown in Figure 6. The calculated $D_T$ and $R_h$ are summarized in Table 2. The $R_h$ of P3, P4, and P5 were in the range of 30–40 nm, and the $R_h$ of PMMA-b-PEO20k-b-PMMA increased slightly with the $M_n$ of PMMA. The $R_h$ of P6, P7, and P8 were much larger than that of P3, P4, and P5 and in the range of 110–170 nm. Moreover, the $R_h$ of PMMA-b-PEO100k-b-PMMA also increased with the $M_n$ of PMMA. Therefore, the $R_h$ of PMMA-b-PEO-b-PMMA increased with the $M_n$ of both PEO and PMMA, and the $M_n$ of PEO showed a much greater influence than the $M_n$ of PMMA.

The microstructures of the triblock copolymers in the dilute aqueous solution were studied from their transmission electron microscopy (TEM) images of the corresponding supernatant solution, and they are summarized in Figure 7. Scheme 1 also shows the schematic association of PMMA-b-PEO-b-PMMA in an aqueous solution. The triblock copolymers self-assembled into polymer micelles in dilute aqueous solution, and bridges were formed among the micelles above the critical percolation concentration. According to the TEM images, all six triblock copolymers formed bridges between the micelles at the concentration of 0.01 wt%. Therefore, the percolation concentration of these six triblock copolymers should be below 0.01 wt%. The formation of bridges between flower micelles in the aqueous solution is beneficial in providing additional viscosity to the rheology modifier for application in enhanced oil recovery. The presence of bridges allowed us to only estimate the diameter of the formed micelles. The diameters of the micelles formed in the P3, P4, and P5 aqueous solution were about 20–30 nm, whereas that formed in the P6, P7, and P8 were about 60–90 nm. PMMA-b-PEO100k-b-PMMA showed bigger micelles than PMMA-b-PEO20k-b-PMMA, which was consistent with the DLS results.

### EXPERIMENTAL SECTION

**Materials.** Poly(ethylene oxide) (PEO) with $M_n = 20k$ or 100k, triethylamine (TEA), dichloromethane (DCM), 4-(dimethylamino)pyridine (DMAP), α-bromo-β-dimethylamino-β-bromide (BIBB), methyl methacrylate (MMA), 2,2′-bipyridyl, CuBr$_2$, ascorbic acid, THF, diethyl ether, and deuterated chloroform (CDCl$_3$) were purchased from Sigma. MMA was purified by passing through a basic Al$_2$O$_3$ column to remove the inhibitors. Other chemicals were used as received.

**Synthesis of Macrominitiator Br–PEO–Br (P1 and P2).** For the preparation of Br–PEO20k–Br (P1) with the $M_n$ of PEO of 20k g/mol, the PEO ($M_n =$ 20k, 100 g, 5 mmol) was dissolved in DCM (400 mL), followed by the addition of TEA (2 g, 20 mmol) and DMAP (2.4 g, 20 mmol). The mixture was cooled to 0 °C in an ice-bath. Then, the solution of BIBB (4.33 g, 20 mmol) in DCM (50 mL) was added dropwise over a 30 min period. The esterification was conducted at room temperature after 24 h. Thus, Br–PEO20k–Br was precipitated in 10-fold of cold diethyl ether under constant stirring. The polymer P1 was filtered and washed three times with diethyl ether, and the white powder P1 was obtained by drying at 40 °C under vacuum for 12 h for 1 day.

For the preparation of Br–PEO100k–Br (P2) with the $M_n$ of PEO of 100k g/mol, the esterification of PEO ($M_n =$ 100k) was performed using the similar procedure as P1. A viscous PEO solution was obtained by dissolving PEO (P1) in DCM (400 mL), followed by the addition of TEA (2 g, 20 mmol) and DMAP (2.4 g, 20 mmol). Then, the solution of BIBB (4.33 g, 20 mmol) in DCM (50 mL) was added dropwise over a 30 min period. The esterification was conducted at room temperature after 24 h. The Br–PEO100k–Br was precipitated in 10-fold of cold diethyl ether under constant stirring. After filtering and washing three times with diethyl ether, the final product P2 was obtained by drying in the oven at 40 °C under vacuum for 12 h.

**Synthesis of PMMA-b-PEO20k-b-PMMA (P3, P4, and P5).** P1 was used as the macrominitiator to synthesize PMMA-b-PEO20k-b-PMMA with various $M_n$ of PMMA blocks via ARGET ATRP. The targeted molecular weight of PMMA blocks in P3, P4, and P5 were 5k, 20k, and 20k g/mol, respectively.
respectively. Br–PEO20k–Br (10 g, 0.5 mmol) was dissolved in the mixture of toluene (100 mL) and methanol (20 mL), followed by the addition of methyl methacrylate (MMA, 5 g for P3, 10 g for P4, and 20 g for P5), bipyridyl (78 mg, 0.5 mmol), and CuBr2 (2 mg, 0.01 mmol). The mixture turned green due to the presence of Cu(II). After purging with nitrogen for 20 min, ascorbic acid (88 mg, 0.5 mmol) was added and the mixture immediately turned brown due to the formation of Cu(I). After purging nitrogen for another 20 min, the temperature was raised to 70 °C to initiate the polymerization. After 24 h, the polymer was precipitated in 10-fold of cold diethyl ether and washed three times with diethyl ether. The final products were obtained by drying at 40 °C under vacuum for 12 h. The molar ratios of MMA

Table 2. $D_T$ and $R_h$ of Supernatant of the Triblock Copolymer Aqueous Solutions Determined by Dynamic Light Scattering (DLS) at Varied Angles

|       | P3   | P4   | P5   | P6   | P7   | P8   |
|-------|------|------|------|------|------|------|
| $D_T$ ($10^{-12}$ m$^2$/s) | 7.90 | 6.59 | 6.22 | 2.20 | 1.92 | 1.48 |
| $R_h$ (nm)  | 31.0 | 37.3 | 39.5 | 111.8| 127.8| 165.3|

Figure 6. Distribution functions of the triblock copolymers from dynamic light scattering.

Figure 7. TEM images of the supernatant of P3, P4, P5, P6, P7, and P8 in dilute aqueous solutions.
monomer to P1 in the ARGET ATRP process for the synthesis of P3, P4, and P5 was 100, 200, and 400, respectively.

**Synthesis of PMMA-b-PEO100k-b-PMMA (P6, P7, and P8).** P2 was used as the macroinitiator to synthesize PMMA-b-PEO100k-b-PMMA with various \( M_n \) of PMMA blocks via ARGET ATRP. The targeted molecular weight of PMMA block in P6, P7, and P8 were 20k, 50k, and 100k g/mol, respectively. P2 Br–PEO100k–Br (10 g, 0.1 mmol) was dissolved in the mixture of toluene (120 mL) and methanol (50 mL), followed by the addition of methyl methacrylate (MMA, 4 g for P6, 10 g for P7, and 20 g for P8), bipyrindyl (78 mg, 0.5 mmol), and CuBr$_2$ (2 mg, 0.01 mmol). The molar ratios of MMA monomer to P2 in the ARGET ATRP process for the synthesis of P6, P7, and P8 were 400, 1000, and 2000, respectively. After purging with nitrogen for 20 min, the polymerization was conducted at 70 °C. After 24 h, the polymer was precipitated in 10-fold of cold diethyl ether and washed twice with diethyl ether. The final products were obtained by drying at 40 °C under vacuum.

**Preparation of Dilute Aqueous Solution of Triblock Copolymers.** Triblock copolymer (50 mg) was dissolved in THF (5 mL), then Millipore water (48 g) was slowly added at a rate of 1 drop every 10 s under vigorous stirring. The THF was removed via rotary evaporation under vacuum at room temperature for 2 h. The final solution was diluted to 50 mL as the stock solution, and an aqueous triblock copolymer solution (0.1 wt %) was obtained. The stock solution was further diluted to prepare various concentrations of triblock copolymers.

**Characterization.** $^1$H NMR spectra were recorded using a Bruker AC-400 NMR at room temperature by dissolving the samples in CDCl$_3$. The Fourier transform infrared spectra (FTIR) were obtained using Bruker Vertex 70. Surface tension was measured via the tensiometer Data Physics DCAT 21 system at room temperature. The dynamic light scattering (DLS) experiments was performed on a Brookhaven BI-200SM goniometer system equipped with a 522-channel 200SM goniometer system. The authors declare no competing financial interest.

**CONCLUSIONS**

The triblock copolymers PMMA-b-PEO-b-PMMA were synthesized via ARGET ATRP with Br–PEO–Br as macroinitiators. The ARGET ATRP reduced the amount of catalyst and sensitivity to oxygen; therefore, the ARGET ATRP is more applicable than traditional ATRP for scale up. Six triblock copolymers PMMA-b-PEO-b-PMMA with different \( M_n \) of PMMA and PEO blocks were synthesized by ARGET ATRP, as confirmed by FTIR and $^1$H NMR. The aqueous solutions and hydrogels of PMMA-b-PEO-b-PMMA were formed via solvent-induced association. Then, the hydrodynamic diameter, surface tension, and morphology of the aqueous solutions were characterized by DLS, tensiometer, and TEM, respectively, and the self-assembled nanostructures consisted of core–shell flower micellar structures.

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