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ORIGINAL PAPER

Synthesis and characterization of AB$_2$-type star polymers via combination of ATRP and click chemistry

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Abstract Homo/miktoarm star polymers were successfully synthesized via combination of the "arm-first" and "coupling-onto" strategies. Firstly, the multifunctional coupling agent (core), 2, 4, 6-tris(3-ethynylphenyl)-1,3,5-triazine-2,4,6-triamine (TPTTA), was synthesized. Secondly, the linear polystyrene-Cl (PS-Cl) and poly(2-(dimethylamino)ethyl methacrylate)-Br (PDMAEMA-Br) were prepared by atom transfer radical polymerization (ATRP) method. Then, the linear PS-Cl and PDMAEMA-Br chains were modified by a nucleophilic substitution reaction with sodium azide. Finally, homo/miktoarm star polymers PS$_3$ and PS(PDMAEMA)$_2$ were designed by click reaction between the core (TPTTA) and the arm precursor (PS-N$_3$ or PDMAEMA-N$_3$). The structures of the PS$_3$, PS(PDMAEMA)$_2$ and the precursors were all characterized by NMR, FT-IR, UV and GPC analysis. Moreover, the self-assembly behaviors of the miktoarm amphiphilic copolymer PS(PDMAEMA)$_2$ was also investigated by transmission electron microscopy (TEM).

Keywords Click chemistry · Atom transfer radical polymerization (ATRP) · Miktoarm amphiphilic copolymers · Self-assembly

Introduction

Star polymers have received increasing attention due to their interesting properties, compact structure and globular shape in comparison with their corresponding linear analogues. Previously, the well-defined star polymers were prepared only by living anionic polymerization method [1], however, which demanded relatively rigorous

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experimental conditions. In recent years, the development of controlled/living radical polymerization (CRP), such as, atom transfer free radical polymerization (ATRP) [2–4], nitroxide mediated radical polymerization (NMP) [5, 6], reversible addition fragmentation chain transfer (RAFT) polymerization [7–9], made the synthesis of well-controlled star polymers relatively convenient and easy. Typically, three strategies, "core-first" [10–14], "coupling-onto" [15, 16] and "arm-first" [17–19], were widely used to prepare star polymers. Among them, the "coupling-onto" method required that the functionality of the coupling agent and the coupling efficiency were both extremely high.

ATRP is one of the most effective CRP techniques to produce chain-end-functionalized polymers with predestined structures. In ATRP systems, the obtained polymers usually captured a halogen atom in each ω-ends of the polymers, which can be successfully converted into other functionalized groups, such as hydroxyl, amino and azide groups [2, 20]. Recently, the cycloaddition reactions between an azide and an alkyne, namely "click chemistry", as termed by Sharpless et al., have also attracted much attention due to their high specificity and efficiency [21, 22]. Several research teams have reported the synthesis of a wide range of functional polymers by a combination of ATRP and "click chemistry". In those processes, the obtained polymer captured with a halogen atom by ATRP can be easily transformed into azides via a nucleophilic substitution reaction. Then, the azide end-functionized polymer can be readily "clicked" with functional alkynes [23–31]. Tunca and his coworkers [32] reported a one-pot synthesis of ABC triblock copolymers of poly(ethylene glycol)-*b*-polystyrene-*b*-poly(methyl methacrylate) (PEG-*b*-PS-*b*-PMMA), and poly(ε-caprolactone)-*b*-polystyrene-*b*-poly(methyl methacrylate) (PCL-*b*-PS-*b*-PMMA) by combining in situ click [3 + 2] and Diels-Alder [33] [4 + 2] reactions. Matyjaszewski's group synthesized the three-arm block copolymer poly(ethylene oxide)-*b*-polystyrene (PEO-*b*-PS)$_3$ by combination of "core-first" and "coupling-onto" strategies [34]. Our group also prepared the well-defined hetero-arm star polymers, containing three polystyrene chains and one poly(methyl methcryate) (PMMA) chain via the combination of RAFT polymerization, ATRP and "click chemistry" methods [35]. However, according to the experimental results reported by Tunca et al. [36], the click reaction efficiency for A$_3$-type star polymer, PS$_3$, has been found to be only 87%. Although the reaction mixture contained mainly A$_3$ star polymer, there was also a small amount of A$_2$ block copolymer and A$_1$ homopolymer. The homogeneous A$_3$-type star polymer (PS$_3$) was not easily obtained due to the difficult detachment of the oil PS linear polymer. The similar results were also observed by Matyjaszewski's group [27, 34]. Therefore, the homogeneous star polymers were not easy to be obtained by "click" coupling reactions.

Miktoarm star polymer is a kind of copolymer in which the arms with different chemical structures were connected at one junction point. Among them, amphiphilic miktoarm star copolymers showed quite different aggregated morphologies in bulk [37–39] and the self-assembly behaviors in solution [40, 41]. Recently, Liu et al. [42] reported the synthesis of well-defined Y-shaped miktoarm amphiphilic copolymers, poly (e-caprolactone)-*b*-(poly(2-(dimethylamino)ethylmethacrylate))$_2$ ((PCL)(PDMA)$_2$) and (PCL)$_2$(PDMA) via a combination of ring-opening polymerization (ROP) and ATRP techniques by the “core-first” method. However, up to now, few publications have been reported about the synthesis of the amphiphilic miktoarm star copolymer by “arm-first” method. Recently, Harruna et al. reported the synthesis of amphiphilic miktoarm tris(2,2′-bipyridine)ruthenium-cored star-shaped polymers consisting of one polystyrene block and two poly(*N*-isopropylacrylamide) blocks using RAFT polymerization. In light of these considerations, herein, we made effort to synthesize a homo/miktoarm A_3/A_2B star polymer via combination ATRP and click reaction. The relatively low efficiency of the click coupling reaction for A_3-type polystyrene was also observed at various temperatures. Furthermore, amphiphilic miktoarm star copolymer PS(PDMAEMA)$_2$ was also successfully prepared using a click reaction between the core (TPTTA) and the arm precursor (PS-N_3 and PDMAEMA-N_3) by “arm-first” method. Most interestingly, the efficiency of the click coupling reaction for AB_2-type PS(PDMAEMA)$_2$ was enhanced by addition of excess hydrophilic precursors (PDMAEMA-N_3). Meanwhile, the spherical micelles could be easily prepared via the self-assembly of amphiphilic miktoarm star copolymers PS(PDMAEMA)$_2$.

Experimental section

Materials

Sodium azide (Alfa Aesar, 98%), 3-aminophenylacetylene (Alfa Aesar, 98%), cyanuric chloride (Acros, USA, 97%), 1-phenylethylchloride (Aldrich, 98%), 9-chloromethylanthracene (Aldrich, 98%), and ethyl-2-bromoisobutyrate (EBIB) (Alfa Aesar, 98%) were used as received. Styrene (St) (chemically pure, Shanghai Chemical Reagent Co. Ltd) was purified by extraction with 5% sodium hydroxide aqueous solution, followed by washing with water and drying with anhydrous sodium sulfate overnight, finally distillated under vacuum. Dimethylaminomethyl methacrylate (DMAEMA) (analytical reagent, Shanghai Chemical Reagent Co. Ltd) was distillated under vacuum. Copper bromide (98%; Aldrich) was stirred with acetic acid for 12 h, washed with ethanol and diethyl ether, and then dried in vacuum. 2, 2′-Bipyridine (bpy) (analytical reagent, Shanghai Chemical Reagent Co. Ltd) was used as received without further purification. *N*, *N*, *N*′, *N*″, *N*″-pentamethyldiethylenetriamine (PMDETA) (98%; Jiangsu Liyang Jiangdian Chemical Factory, Liyang, China) was dried with 4-Å molecular sieve and distilled in vacuum. *N*, *N*-dimethyl formamide (DMF) (analytical reagent, Shanghai Chemical Reagent Co. Ltd) were distillated under vacuum in order to get reproducible results for click reaction and ATRP every time. Other solvents were all analytical grade and used as received without further purification.

Instrumentation

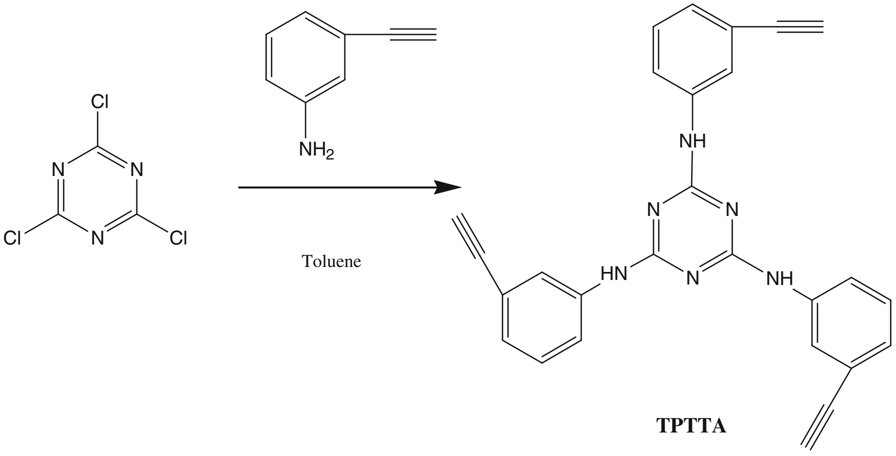
^1H NMR spectra were recorded on an INOVA 400 MHz nuclear magnetic resonance (NMR) instrument, using $CDCl_3$ or dimethylsulfoxide-D_6 (DMSO-d_6) as the solvent and tetramethylsilane (TMS) as the internal standard at ambient temperature. The fluorescence emission spectra of the polymers were obtained on an Ediburger FLS920 fluorescence spectrophotometer at room temperature. Ultraviolet visible (UV–vis) absorption spectra of the polymers in THF solutions were performed on a Shimadzu (Kyoto, Japan) UV-240 recording spectrophotometer at ambient temperature. FT-IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer. The elemental analyses for C, H, and N were tested by a LECO-CHNS microanalyzer. Transmission electron microscopy (TEM) was recorded on a Tecnai G^2-20 TEM at a 200 kV accelerating voltage. The samples were prepared by mounting a drop of the micelle solution (0.05 mL) on a copper EM grid covered with a thin film of formvar. The molecular weights and molecular weight distributions of the polymers were determined with a Waters 1515 gel permeation chromatography (GPC) equipped with refractive index detector, using HR1, HR3, and HR4 column with molecular weight range 100–500000 calibrated with PS standard samples. THF was used as the eluent at a flow rate of 1.0 mL min^{-1} operated at 30 °C. The conversion of the monomers was determined gravimetrically.

Synthesis of 2, 4, 6-tris (3-ethynylphenyl)-1, 3, 5-triazine-2, 4, 6-triamine (TPTTA)

3-aminophenylacetylene (2.34 g, 20 mmol) was added dropwise to a solution of cyanuric chloride (3.68 g, 20 mmol) in toluene (100 mL) in a round-bottom flask over 20 min. The solution was stirred for 1 h under 0–5 °C. Then the mixture was heated to 40 °C, and 3-aminophenylacetylene (5.85 g, 50 mmol) was again added dropwise to the mixture within 5 min. Then the reaction mixture was stirred at 110 °C overnight. The mixture was directly filtered, and the solvent was removed by rotary evaporation under vacuum. The obtained crude product was purified by a silica gel column with the mixture of petroleum ether and ethyl acetate (3/1, *v*/*v*). The product was obtained as white solid (5.52 g, yield: 64%). The relevant analytical data are as follows: Elemental Analysis: Calculated (%): C 76.04, H 4.25, N 19.71; Found(%): C 76.09, H 4.14, N 19.45. ^{1}H NMR (DMSO-d_6), δ): 9.41 (s, 3H), 7.11-7.92 (m, 12H), 4.19 (s, 3H) (Scheme 1).

Synthesis of polymers captured with halogen atoms and azide groups

The polystyrene-Cl (PS-Cl) was prepared by ATRP method using 9-chloromethylanthracene or 1-phenylethylchloride as the initiator, and CuCl/bpy or CuCl/PMDETA as the catalyst system, respectively. Poly(2-(dimethylamino)ethyl methacrylate)-Br (PDMAEMA-Br) was prepared using ethyl-2-bromoisobutyrate as the initiator and CuBr/PMDETA as the catalyst system [43]. A typical ATRP procedure initiated by 9-chloromethylanthracene was carried out as follows: St (1 mL, 8.71 mmol) and 9-chloromethylanthracene (19.75 mg, 0.0871 mmol) was added to a dry ampoule filled with copper chloride (17.33 mg, 0.1742 mmol), bpy (81.4 mg, 0.522 mmol) and solvent tetrahydrofuran (THF) or toluene (1 mL) (Table 1 (entries 1–2)).The contents were purged with argon for approximately



Scheme 1 The synthetic routes of 2, 4, 6-tris(3-ethynylphenyl)-1,3,5-triazine-2,4,6-triamine (TPTTA)

Table 1 Results of the solution ATRPs of St and DMAEMA

Entry	$[\text{monomer}]_0/[\text{initiator}]_0/[\text{CuX}]_0/[\text{ligand}]_0$	$M_{n(GPC)}$/Conversion (%)/Time(h)	$M_{n(th)}$ (g/mol)	$M_{n(NMR)}$ (g/mol)	M_w/M_n
1	100:1:2:6[a]	4000/32/12	3400	3600	1.49
2	100:1:2:6[b]	9200/85/21	8900	8800	1.29
3	100:1:2:6[b]	4500/41/12	4300	4300	1.20
4	100:1:2:6[c]	3200/30/12	3100	3200	1.22
5	50:1:2:6[d]	2300/28/4	2200	2200	1.10

[a] Monomer: styrene; initiator: 9-chloromethylanthracene; catalyst: CuCl; ligand: bpy; solvent: toluene; $T = 110$ °C

[b] Monomer: styrene; initiator: 9-chloromethylanthracene; catalyst: CuCl; ligand: bpy; solvent: THF; $T = 110$ °C

[c] Monomer: styrene; initiator: 1-phenylethylchloride; catalyst: CuCl; ligand: PMDETA; solvent: THF; $T = 110$ °C

[d] Monomer: DMAEMA; initiator: EBIB; catalyst: CuBr; ligand: PMDETA; solvent: THF; $T = 60$ °C

10 min to eliminate oxygen. Then, the ampoule was flame sealed and placed in an oil bath at a desired temperature. After certain reaction time (Table 1), each ampoule was quenched in ice water, and then opened. The contents was diluted with about 2 mL of THF, and then precipitated into about 250 mL of petroleum ether twice. The polymer was collected by filtration and dried under vacuum for 24 h at room temperature. The end-functionalized polystyrene-N_3 (PS-N_3), and poly(2-(dimethylamino)ethyl methacrylate)-N_3 (PDMAEMA-N_3) were prepared by the nucleophilic substitution reaction between previously obtained PS-Cl or PDMAEMA-Br and sodium azide. The following procedure of preparing azido-terminated polystyrene (PS-N_3) was typical: the obtained linear polymer PS-Cl (2 g, 0.465 mmol) was dissolved in *N*, *N*-dimethylformamide (DMF) (15 mL), water

(2 mL), NaN_3 (1.51 g, 23.25 mmoL) and NH_4Cl (24.8 mg, 0.465 mmoL) was added as phase transfer catalyst (PTC) [44], and then, the mixture was allowed to stir at 60 °C overnight. Then the mixture was precipitated into methanol/water mixture (*v*/*v* = 1/1) and washed with deionized water three times. The ω-azide end-functionalized polymers (PS-N_3) were thus obtained. The PDMAEMA-N_3 was also prepared by the similar procedures as described above.

Synthesis of three-armed polymer (PS_3) and amphiphilic miktoarm AB_2 star polymer ($PS(PDMAEMA)_2$) by click coupling reactions

Three-armed polystyrene (PS_3) were prepared by click coupling reaction between the linear polymer (PS-N_3, prepared using 9-chloromethylanthracene as the initiator) and coupling agents (TPTTA), catalyzed by CuCl/PMDETA complex. A typical reaction conditions with the ratio of reagents $[PS\text{-}N_3]_0/[TPTTA]_0/[CuCl]_0/[PMDETA]_0 = 3{:}1{:}3{:}3$ are briefly described. PS-N_3 (1 g, 0.232 mmoL), TPTTA (3.31×10^{-3} g, 7.75×10^{-2} mmoL), CuCl (2.31×10^{-3} g, 0.232 mmoL) and PMDETA (4.01×10^{-2} g, 0.232 mmoL) were added to a dry ampoule filled with 5 mL of DMF solvent which was degassed by three freeze-pump-thaw cycles, then the reaction mixture was purged with argon for approximately 10 min to eliminate the oxygen. Then, the ampoule was flame sealed and placed in an oil bath at designed temperature (110 °C) for 24 h. The polymer solution was allowed to pass through an Al_2O_3 column to remove the copper salt, and precipitated in about 250 mL methanol. Then the polymer was filtered and dried at 50 °C in a vacuum oven for 24 h. When click coupling reaction between linear polymer (PS-N_3, prepared using 1-phenylethylchloride as the initiator) and TPTTA was conducted, the reaction temperature was controlled at 70 °C.

The procedures of synthesizing the amphiphilic miktoarm AB_2 star polymer $PS(PDMAEMA)_2$ were as follows: PS-N_3 prepared using 9-chloromethylanthracene as the initiator (1 g, 0.112 mmoL), PDMAEMA-N_3 1.24 g, 0.561 mmoL), TPTTA (4.79×10^{-2} g, 0.112 mmoL), CuCl (3.34×10^{-2} g, 0.336 mmoL) and PMDETA (5.81×10^{-2} g, 0.336 mmoL) were added to a dry ampoule filled with 5 mL of DMF which was degassed by three freeze-pump-thaw cycles, then the reaction mixture was purged with argon for approximately 10 min to eliminate oxygen. Then the ampoule was flame-sealed and placed in an oil bath held by a thermostat at 70 °C for 24 h. The polymer solution was allowed to pass through an Al_2O_3 column to remove the copper salt, precipitated in methanol and water (*v*/*v* = 1/1) to remove linear PDMAEMA or star $(PDMAEMA)_3$ due to the solubility of those polymers in both solvents. The product was dried in a vacuum oven at 50 °C.

Preparation of the micelle solutions

The amphiphilic miktoarm AB_2 star copolymer, $PS(PDMAEMA)_2$ (5 mg), was dissolved in 1 mL of dry THF at room temperature to obtain a 5 mg/mL polymer solution. Then the polymer solution was added into 5 mL of deionized water at a rate of one drop every 10 s by a microsyringe under vigorous stirring.

Results and discussions

Synthesis of PS-N_3 and PDMAEMA-N_3

The well-defined linear PS-Cl were prepared via solution ATRP of St initiated by 9-chloromethylanthracene in the presence of CuCl/bpy ($[\text{monomer}]_0/[\text{initiator}]_0/[\text{CuCl}]_0/[\text{bpy}]_0 = 100{:}1{:}2{:}6$). The results were presented in Table 1 (entries 1–3). As seen in Table 1, the type of the solvent had significant effect on the polymerization. The molecular weight distributions of the obtained polymers in THF were narrower than those in toluene. Meanwhile, the $M_{n(GPC)}$s were very close to the theoretical values ($M_{n(th)}$s) ($M_{n(th)} = ([M]_0/[I]_0) \times M_M \times \text{Conversion} + M_I$, where $[M]_0$ and $[I]_0$ are initial concentrations of monomer and initiator, respectively, and M_M and M_I are the molecular weight of St and the initiator, respectively.), which indicated the relatively high apparent initiation efficiencies f (defined as $M_{n(th)}/M_{n(GPC)}$). In addition, the well-defined PS-Cl can be also prepared using 1-phenylethylchloride as the initiator and CuCl/PMDETA as the catalyst system. Meanwhile, the well-defined PDMEMA-Br was also successfully prepared via ATRP using EBIB as the initiator and CuBr/PMDETA as the catalyst as shown in Table 1 (entry 5).

The well-defined ω-azide-ends of polymers (PS-N_3) were successfully prepared by the reaction between previously obtained PS-Cl (prepared using 9-chloromethylanthracene as the initiator) and sodium azide. The structure of azide end-capped polystyrene (PS-N_3) was investigated by ^{1}H NMR spectra as shown in Fig. 1. From

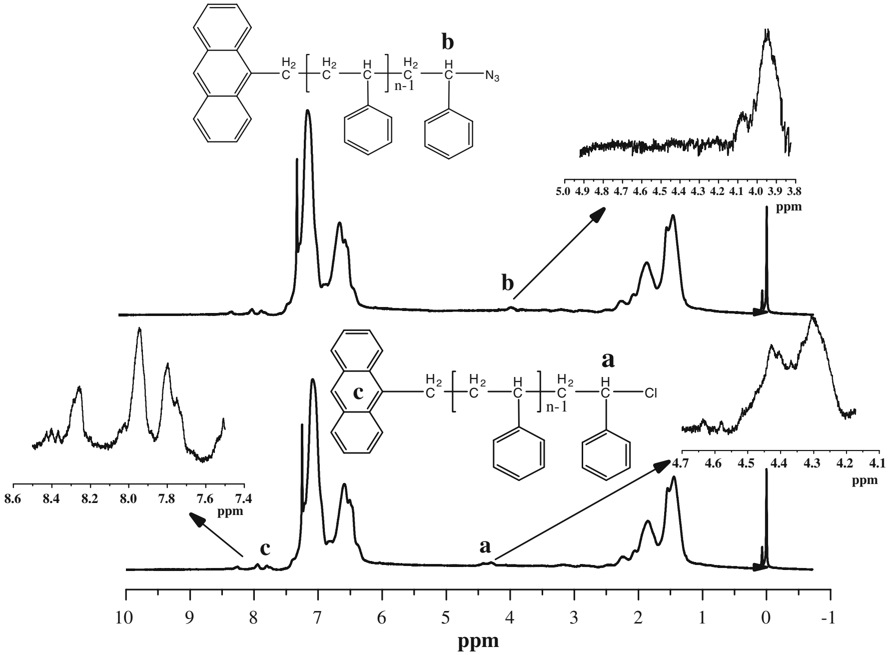
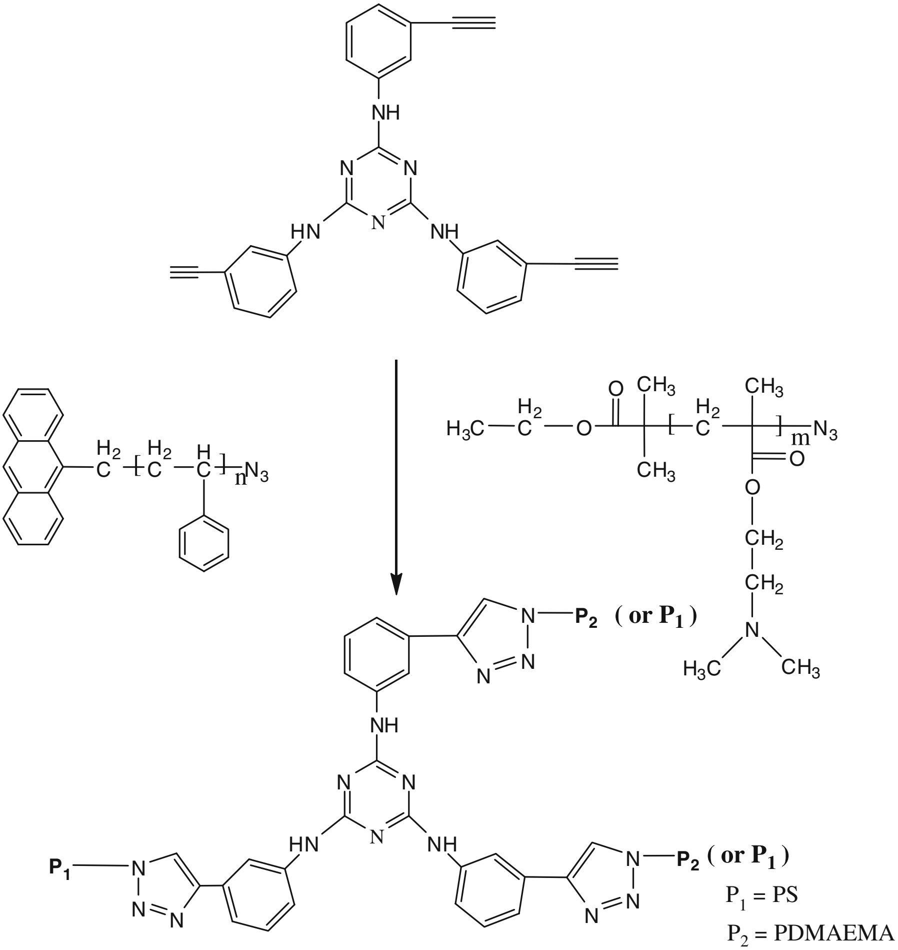


Fig. 1 ^{1}H NMR spectra of the polymers (PS-Cl and PS-N_3). PS-Cl: $M_{n(GPC)} = 4500$ g/mol, $M_w/M_n = 1.20$; PS-N_3: $M_{n(NMR)} = 4500$ g/mol, $M_w/M_n = 1.19$

Fig. 1, we can see that the characteristic signals at 7.50–8.50 ppm were attributed to the anthryl protons (c) from PS chains. Meanwhile, the signal at 4.40 ppm, assigned to methyne proton next to the terminal chloro of PS, disappeared, and a new peak at 3.95 ppm, attributed to methyne proton next to the terminal azide of PS (PS-N_3) appeared. Furthermore, the characteristic signal at 2100 cm^{-1} of azide group was observed from FT-IR spectroscopy in Fig. 5a. The results above showed that the chloro end-capped polystyrene (PS-Cl) was quantitatively converted to azide end-capped polystyrene (PS-N_3). These results indicated that the functional anthryl and azide groups were both attached to the polymer chain ends and the substitution was complete. Meanwhile, the appearance of the characteristic signal of the azide group at about 2100 cm^{-1} (Fig. 5b) also confirmed the successful preparation of PDMEMA-N_3.

Preparation of the three-armed polystyrene (PS$_3$)

The three-armed polystyrene was obtained by the coupling-onto method using a click-chemistry strategy (Scheme 2), which were carried out with equimolar amounts of the reactants ([azide group]/[trisyne group] = 3/1) in DMF with CuCl/PMDETA as the catalyst system for about 24 h. The gel permeation chromatography (GPC) was used to trace the process of the reaction (Fig. 2). The GPC curves showed a decrease in retention time with the increasing reaction time (24 h). However, on the GPC curves multiple peaks emerged when the click reaction was carried out at a relatively high temperature (110 °C). For the star polymer, the $M_{n(GPC)}$ are always much smaller than those for theory due to relative smaller hydrodynamic size than linear counterparts with the same molecular weight. However, from the GPC results, the molecular weight of the peak in the GPC trace centered at around 15.5 min have increased to around 600000 g/mol, although this molecular weight goes beyond the range of measure. And the molecular weight of the peak in the GPC trace centered at around 17.5 min was about 38,000 g/mol. It was very difficult to find the according peak of the three-armed polystyrene. These may be due to a side-reaction between anthracene-anthracene (or other) end-group side reactions [45]. To confirm the existence of the side-reaction in the click system above, we used the PS-N_3 prepared via ATRP using 1-phenylethylchloride as the initiator to carry out the similar click reaction with TPTTA at two different temperatures. The results were shown in Fig. 3. From GPC traces, it was clearly observed that monodispersive polymers were obtained at a high temperature (110 °C). However, there was an apparent tail in GPC traces, which indicated the obtained polymer maybe contain the star polymer (PS$_3$) and/or linear polymer (PS$_2$). At a relatively low temperature (70 °C), the tail in GPC traces became inconspicuous, which implied a relatively high efficiency of the click reaction at 70 °C. However, when the click reaction between PS-N_3 (prepared using 9-chloromethylanthracene as initiator) and TPTTA was carried out at 70 °C, it was hard to obtain PS$_3$ star polymer (Fig. 4).



Scheme 2 The synthetic route of star polymers of PS_3 and $PS(PDMAEMA)_2$

Synthesis of the amphiphilic miktoarm AB_2 star polymer $PS(PDMAEMA)_2$

We also synthesized the amphiphilic miktoarm AB_2 star polymer $PS(PDMAEMA)_2$ using the click reaction between TPTTA with PS-N_3 (prepared from PS-Cl synthesized via ATRP using 9-chloromethylanthracene as initiator) and PDMAEMA-N_3 ($[PS\text{-}N_3]_0$:$[PDMAEMA\text{-}N_3]_0$:$[TPTTA]_0 = 1{:}5{:}1$; PS-N_3: $M_{n(GPC)} =$ 9200 g/mol, PDMAEMA-N_3:$M_{n(GPC)} = 2300$ g/mol) as shown in Scheme 2. The reaction catalyzed by the CuCl/PMDETA system was carried out at 70 °C for 24 h and the polymer solution was allowed to pass through an Al_2O_3 column to remove the copper salt, precipitated in methanol and water ($v/v = 1/1$) to remove linear PDMAEMA or star $(PDMAEMA)_3$ due to the solubility of those polymers in both solvents. The obtained amphiphilic miktoarm AB_2 star polymer $PS(PDMAEMA)_2$ was confirmed by FT-IR, ^{1}HNMR, GPC, ultraviolet absorption and fluorescence

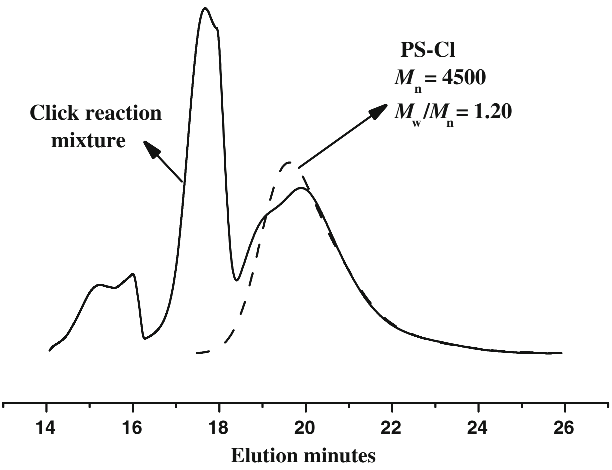


Fig. 2 GPC curves of PS-Cl prepared via ATRP using 9-chloromethylanthracene as the initiator and the click-reaction mixture of PS-N_3 and TPTTA at 110 °C for 24 h

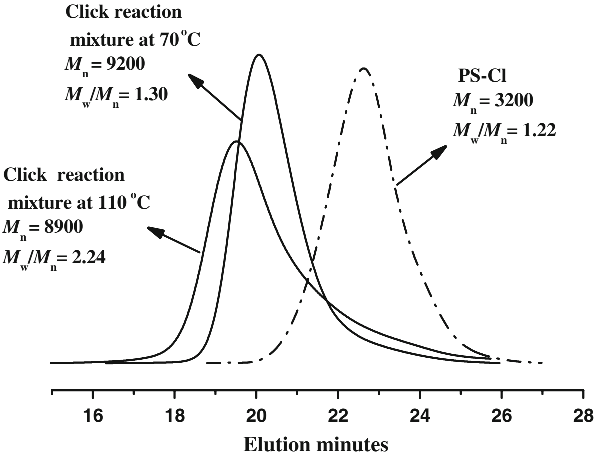


Fig. 3 GPC curves of PS-Cl prepared via ATRP using 1-phenylethylchloride as the initiator and the click-reaction mixture of PS-N_3 and TPTTA at different temperatures

spectra as shown in Figs. 5, 6, 7, 8, 9. The characteristic absorption peaks of the terminal azide group at 2093 cm^{-1} were observed in the FT-IR spectra of the polymers (PS-N_3) and (PDMAEMA-N_3) completely disappeared in the obtained amphiphilic miktoarm AB_2 star polymer PS(PDMAEMA)$_2$. Furthermore, the FT-IR results further confirmed the existence of PS chain (the characteristic absorption peak at ~697, 1452 and 1492 cm^{-1}) and PDMAEMA chain (the absorption peak at 1729 cm^{-1} ascribed to the vibration of C=O in DMAEMA unit).

The obtained amphiphilic miktoarm AB_2 star polymer PS(PDMAEMA)$_2$ were also analyzed by ^1H NMR spectroscopy as presented in Fig. 6. In Fig. 6, the

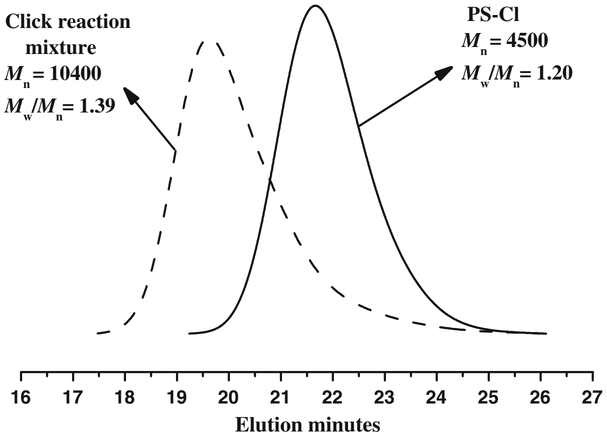


Fig. 4 GPC curves of PS-Cl prepared via ATRP using 9-chloromethylanthracene as initiator and the click-reaction mixture of PS-N_3 and TPTTA at 70 °C

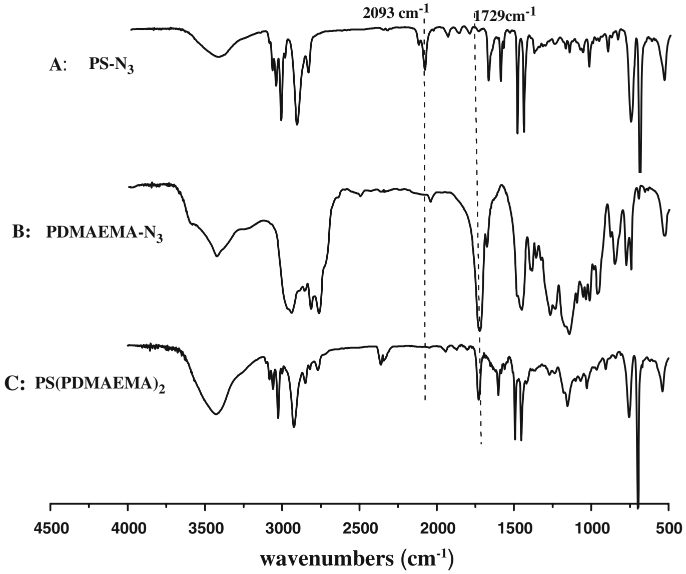


Fig. 5 FT-IR spectra of the linear polymers (PS-N_3 and PDMAEMA-N_3) and the amphiphilic miktoarm AB_2 star polymer PS(PDMAEMA)$_2$. PS-N_3: $M_{n(GPC)} = 9200$ g/mol, $M_w/M_n = 1.29$; PDMAEMA-N_3: $M_{n(GPC)} = 2300$ g/mol, $M_w/M_n = 1.10$; (PS(PDMAEMA)$_2$: $M_{n(GPC)} = 12900$ g/mol, $M_w/M_n = 1.31$

characteristic signals at around 7.50–8.32 ppm (d in Fig. 6) are assigned to the anthracene ring protons from PS chain. Furthermore, the relative composition of the PS to PDMAEMA segments in the amphiphilic miktoarm AB_2 star polymer (PS(PDMAEMA)$_2$) was close to the ratio of 1/2, which was derived from ^{1}H NMR spectra, that is, the integration of the aromatic proton in St units (c in Fig. 6, $\delta = 6.25$–7.24 ppm) to the methylene proton close to oxygen of DMAEMA unit

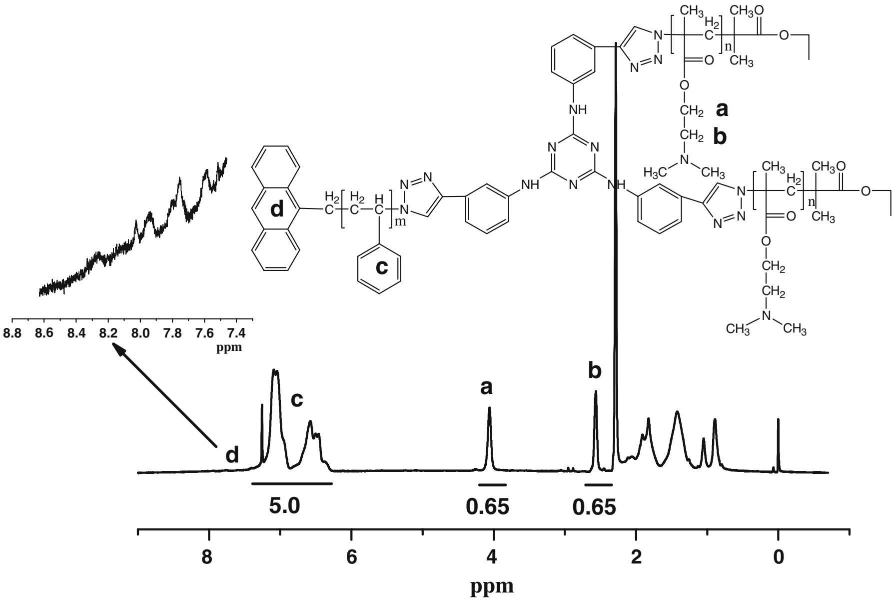


Fig. 6 ^{1}H NMR spectrum of the amphiphilic miktoarm AB_2 star polymer $PS(PDMAEMA)_2$ in $CDCl_3$. $PS(PDMAEMA)_2$: $M_{n(GPC)} = 12900$ g/mol

(a in Fig. 6, $\delta = 4.00–4.10$ ppm). Furthermore, the molecular weight of $PS(PDMAEMA)_2$ can be calculated from Fig. 6 ($M_{n(NMR)} = 13300$ g/mol, by Eq. 1), which was close to the value measured by GPC ($M_{n(GPC)} = 12900$ g/mol). These results above indicated that the amphiphilic miktoarm AB_2 star polymer $PS(PDMAEMA)_2$ were successfully prepared via the one-pot click reaction.

$$M_{n(NMR)} = \left((I_{4.00-4.10}/2)/(I_{6.25-7.24}/5)\right) * \left(M_{n(NMR),PS}/MW_{st}\right) * MW_{DMAEMA} + M_{n(NMR),PS} \qquad (1)$$

$I_{4.00–4.10}$: the integral of the signals at 4.00–4.10 ppm;
$I_{6.25–7.24}$: the integral of the signals at 6.25–7.24 ppm;
$M_{n(NMR), PS}$: the NMR number-average molecular weight of PS;
MW_{St}: molecular weight of St;
MW_{DMAEMA}: molecular weight of DMAEMA.

GPC curves of the original PS-Cl (prepared using 9-chloromethylanthracene as initiator), PDMAEMA-Br and the click-reaction product $PS(PDMAEMA)_2$ are shown in Fig. 7. The GPC trace of the amphiphilic miktoarm AB_2 star polymer $PS(PDMAEMA)_2$ displayed a narrow molecular weight distribution ($M_w/M_n = 1.31$) and a clear shift toward higher elution time. Moreover, the GPC molecular weight was close to the calculated value from ^{1}H NMR. All the results indicated that the well-controlled amphiphilic miktoarm AB_2 star polymer $PS(PDMAEMA)_2$ was successfully obtained by the click reaction.

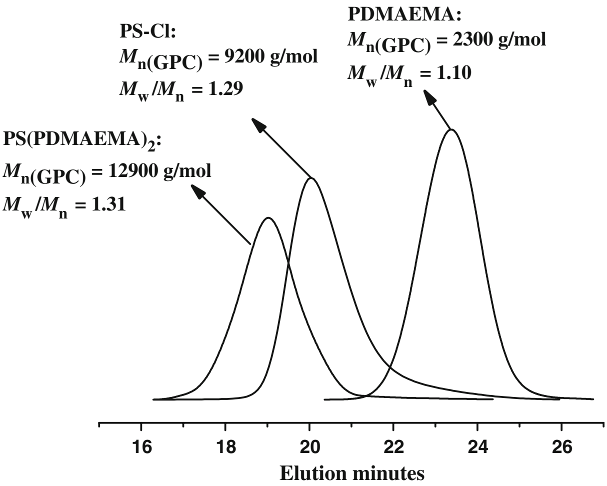


Fig. 7 Typical GPC traces of linear polymers (PS-Cl and PDMAEMA-Br) and the click-reaction production (PS(PDMAEMA)$_2$)

Due to the high sensitivity of the anthracene groups to the UV light, the UV absorption of the PS-Cl, the amphiphilic miktoarm AB_2 star polymer PS(PDMAEMA)$_2$ and the blank sample PDMAEMA in THF were measured as shown in Fig. 8. From Fig. 8, it can be found that both PS-Cl and the amphiphilic miktoarm AB_2 star polymer PS(PDMAEMA)$_2$ showed strong absorptions at around 352, 372 and 392 nm, which were corresponding to the absorptions of the anthracene moieties in the polymer chains. Furthermore, the strong fluorescence emissions of anthracene moieties in the solution also can be observed. The fluorescence emissions of PS-Cl and the amphiphilic miktoarm AB_2 star polymer PS(PDMAEMA)$_2$ and the blank

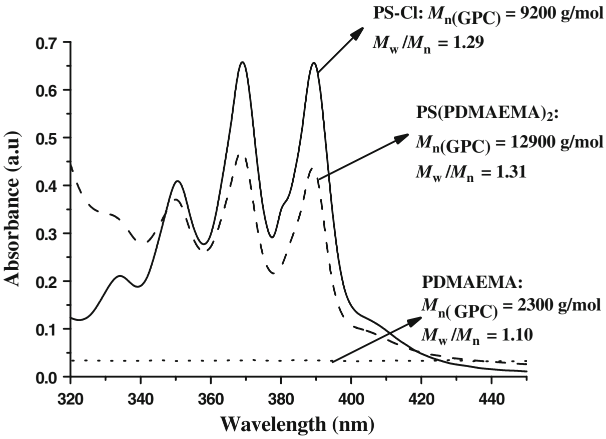


Fig. 8 Ultraviolet absorption spectra of the linear polymers (PS-Cl and PDMAEMA-Br) and the amphiphilic miktoarm AB_2 star polymer PS(PDMAEMA)$_2$. Concentration of all the polymers are 5.0×10^{-5} M with THF as a solvent

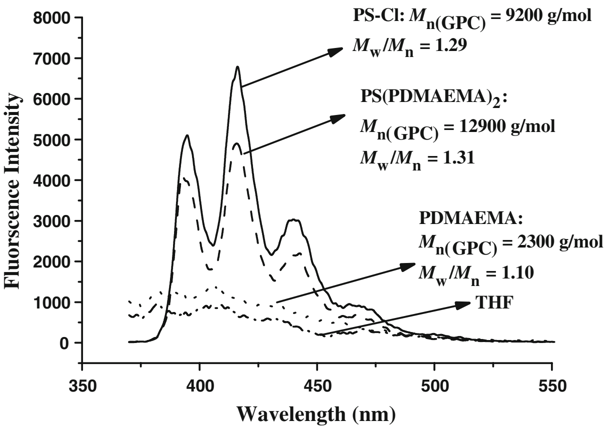


Fig. 9 Fluorescence spectra of the linear polymers (PS-Cl and PDMAEMA-Br) and the amphiphilic miktoarm AB_2 star polymer PS(PDMAEMA)$_2$. Concentration of all the polymers are 5.0×10^{-5} M with THF as a solvent. ($\lambda_{ex} = 380$ nm)

sample PDMAEMA in THF are shown in Fig. 9. It can be observed that PS-Cl and PS(PDMAEMA)$_2$ exhibited strong fluorescence in a wide range of wavelengths in THF at room temperature ($\lambda_{ex} = 380$ nm). The maximum emission wavelength was at around 414 nm, which was consistent with the results reported [46]. Therefore, the obtained amphiphilic miktoarm AB_2 star copolymers were additionally endowed with fluorescent group, which would extend the potential application field of obtained copolymers, such as fluorescence-labeled micelles [47].

Micellization of the obtained amphiphilic miktoarm star polymer PS(PDMAEMA)$_2$

Water-soluble PDMAEMA and its copolymers have generated considerable interest in recent years due to their special temperature/pH-responsive properties, which is especially suitable for gene delivery materials [48–51]. In this part, we described the formation of aggregates of the obtained amphiphilic miktoarm star polymer PS(PDMAEMA)$_2$. Typical TEM images of the aggregates are shown in Fig. 10. From Fig. 10, we can find that the spherical micelles composed of a hydrophobic core (PS) and a hydrophilic shell (PDMAEMA) were successfully prepared. The image showed that all the particles are almost spherical and the mean diameter is about 200.0 nm.

Conclusions

The well-defined amphiphilic miktoarm star copolymer PS(PDMAEMA)$_2$ was successfully prepared by the arm-first technique via click reaction between a novel trifunctional core (TPTTA) with the linear polymeric chains PS-N_3 and

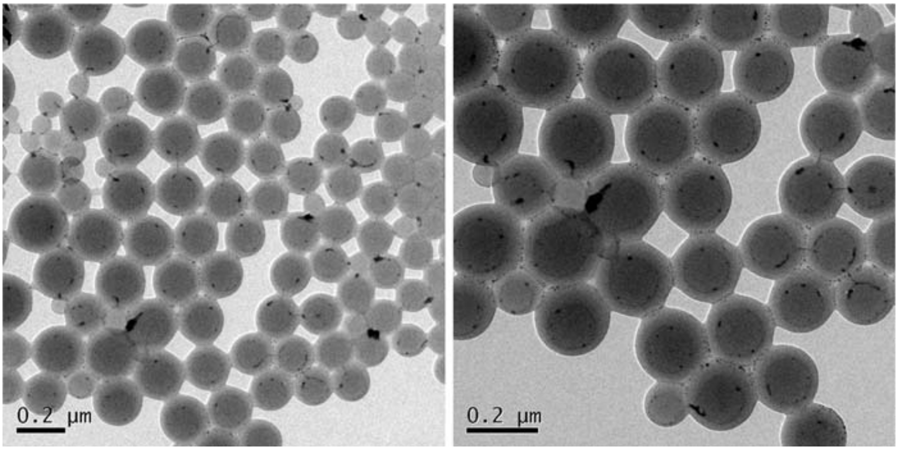


Fig. 10 TEM images of amphiphilic miktoarm star polymer PS(PDMAEMA)$_2$ formed on copper netting by casting the micelle solution at room temperature

PDMAEMA-N$_3$. The obtained amphiphilic miktoarm star copolymer PS(PDMAEMA)$_2$ showed typical optical properties of the anthracene moieties, such as fluorescence and UV absorption. Furthermore, the spherical micelles were also successfully prepared via self-assembly technique.

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