Macromolecules

Thermoresponsive AIE-Active Miktoarm Star Polymers: Precise Synthesis and Structure-Dependent Photoluminescence

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ABSTRACT: Implementing a macromolecular engineering strategy for thermoresponsive fluorescence polymers is an important approach to a wide-range tunable photoluminescence behavior that meets the requirement of various application scenarios. Herein, three tetraphenylethylene (TPE) derivatives bearing different numbers of bromopropionate and hydroxyl groups were synthesized with simplicity and efficiency. After Cu(0)-mediated singleelectron transfer living radical polymerization (SET-LRP) of methyl acrylate (MA), functional group conversion of hydroxyl groups to trithiocarbonate groups, and mechanistic transition to reversible addition—fragmentation chain transfer (RAFT) polymerization of 2-(dimethylamino)ethyl methacrylate (DMAEMA),



aggregation-induced emission-active miktoarm star TPE-(PMA)_n-(PDMAEMA)_{4-n} (n = 1-3) with a well-defined macromolecular structure were synthesized. Owing to the upper critical solution temperature (UCST) behavior of the PMA arm, TPE-(PMA)_n-(PDMAEMA)_{4-n} displayed an intriguing thermoresponsive emission behavior in EtOH/H₂O mixtures. The macromolecular structure had a profound influence on the performance of TPE-(PMA)_n-(PDMAEMA)_{4-n} delivering highly differentiated fluorescence thermoresponsiveness. The underlying mechanism was revealed based on variable-temperature ¹H nuclear magnetic resonance and dynamic laser scattering. The knowledge gained in our work is important for the rational design and application of a thermoresponsive intelligent fluorescence system.

INTRODUCTION

Thermoresponsive aggregation-induced emission (AIE)-active polymers are a type of intelligent material system that can "compile" thermo stimulus in the outer environment into a facilely detectable fluorescence signal according to the AIE mechanism.¹ Owing to their fascinating responsive behavior and the simplicity in the regulation of temperature, they have drawn great research interest and demonstrated widespread potential applications as smart therapeutic delivery carriers,² fluorescent thermometers,^{3–6} intracellular temperature sensors,^{7–9} intracellular imaging,^{10,11} etc.

The most popular synthetic strategy for thermoresponsive AIE polymers is through integrating AIE luminogens (AIEgen) and thermoresponsive polymers.^{12–21} These studies primarily focused on constructing a specific type of chain architecture for AIE-active polymers with lower critical solution temperature (LCST) behavior, as well as their utilization in diverse application scenarios.^{13–16} Nevertheless, AIE-active polymers with an upper critical solution temperature (UCST) behavior have rarely been explored. Jia et al.²² have incorporated tetraphenylethylene (TPE) into the copolymer of cholic-acid-appended acrylamide and acrylamide (Am), obtaining an AIE-active UCST polymer. The polymer displays the quenching of fluorescence when the temperature is increased beyond its UCST, and all chains are dissociated. Liu et al.²³ have applied

the clusterization-triggered emission (CTE) mechanism in constructing a luminescent UCST polymer by the copolymerization of acrylic acid (AA) and N-vinylcaprolactam (NVCL). The temperature can be regulated to tune the hydrogen-bonding-based chain association, thus bringing about a thermoresponsive emission behavior in aqueous solutions. These pioneering works call for unleashing the great potential of AIE-active UCST polymers by enriching their structural diversity to achieve a highly tunable thermoresponsive fluorescence behavior on both the "sensing" and "signaling" sides.

Miktoarm star polymers are a unique class of star-shaped polymers with various types of constituent polymer arms being connected to a joint core.^{24–30} Due to their thermodynamically immiscible arms and special chain architecture, miktoarm star polymers can exhibit peculiar self-assembling behavior and attractive performance in various aspects.³¹ Therefore, they

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have shown great promise as therapy delivery carriers,^{32–34} stimuli-responsive platforms,^{24,35,36} catalytic nanoreactors,³⁷ antimicrobial agents,^{38,39} and so on. In the development of stimuli-responsive miktoarm star polymers, it has been found that tunable properties can be attained by precisely tailoring their structural parameters (the number and chain length of different arms). For example, AB₂ miktoarm star polymers (A = polyethylene glycol; B = polyglutamic acid) with doxorubicin (DOX) conjugated via a hydrazone linker have been found to display higher DOX loading and faster release kinetics at pH = 5.0 compared to their linear analogues (AB polymers).⁴⁰ Wang et al.⁴¹ have prepared A₂B-, A₂B₂-, A₃B-, and AB₃-type amphiphilic miktoarm star copolymers (A = $poly(\varepsilon$ -caprolactone); B = poly(ethylene glycol) monomethyl ether methacrylate), where the A₃B-type micelles have reduced critical micelle concentration, enhanced DOX encapsulation efficiency, and improved therapeutic efficiency. Concerning thermoresponsive AIE-active miktoarm star polymers, Zhang and Hadjichristidis⁴² have prepared (PE)_n-(PtBMA)_m-P(TPE-2St) and $(PE)_n$ -(PMAA)_m-P(TPE-2St), which exhibit increasing photoluminescence (PL) intensity with increasing temperature. However, these miktoarm star polymers were synthesized by the "arm-first" approach with TPE-2St as a crosslinker, thus bearing an inaccurate number of different constituent arms and widely distributed microenvironments around each TPE moiety.

To boost the development of AIE-active polymers with superior properties for advanced applications, it is crucial to enrich their structural diversity and complexity with macromolecular engineering. This is essential for gaining a fundamental understanding of the correlation between the highly differentiated stimuli-responsive fluorescence behavior of AIE-active polymers and variations in their macromolecular structure including molecular weight, copolymer composition, topology, and positioning of AIEgens. Previously, our group has developed TPE-appended maleic acid copolymers as a multistimuli-responsive AIE-active polymer platform, with their sensing and signaling behavior influenced prominently by different comonomers⁴³ and chain topology.⁴⁴ Besides, we have synthesized AIE-active TPE-(polymethyl acrylate)_n and TPE-(poly(acrylic acid)) $_n$ (n = 1-4), which demonstrate stronger emission with larger n (more arms).⁴⁵ Herein, we raise a fundamental question: in what way will the structural parameters of UCST-type miktoarm star polymers (respective of arm number) influence their emission behavior if an AIEgen is included in the core?

Aiming to address this question, we developed a very simple "core-first" approach to synthesize AIE-active AB3-, A2B2-, and A₃B-type miktoarm star polymers with great precision. The synthetic strategy involves performing the synthesis of different multifunctional initiators in one pot, Cu(0)-catalyzed single electron transfer-living radical polymerization (SET-LRP),⁴⁶⁻⁵⁰ conversion of hydroxyl groups to trithiocarbonate groups, and reversible addition-fragmentation chain transfer (RAFT) polymerization in cascade. This synthetic strategy avoids multiple protection/deprotection reactions usually required in constructing the multifunctional initiator for a core-first approach.^{41,51-53} UCST-type AIE-active miktoarm star TPE-(polymethacrylate)_n-(poly(N,N-dimethylaminoethyl methacrylate))_{4-n} (TPE-(PMA)_n-(PDMAEMA)_{4-n} (n = 1-3)) were synthesized with precision and subjected to detailed investigation on the thermoresponsive fluorescence behavior in EtOH/H₂O mixtures. Results showed the remarkable effects of the macromolecular architecture on fluorescence thermoresponsiveness. The insights obtained in the present work demonstrate the great value of macromolecular architecture control for developing thermoresponsive fluorescent polymers with sensitive, wide-range adjustable, and highly stable characteristics.

EXPERIMENTAL SECTION

Materials. All materials were used as received unless otherwise stated: tetrakis(4-hydroxyphenyl)ethylene (98%, Bidepharm), ethylene carbonate (99%, Innochem), 2-bromopropionyl bromide (98%, Adamas-beta), tris[2-(dimethylamino)ethyl]amine (Me₆-TREN, 98%, Energy Chemical), dimethyl sulfoxide (DMSO, 99.9%, Alfa Aesar), copper(0) wire of 1.0 mm diameter (99.9%, Alfa Aesar), triethylamine (TEA, >99.9%, Alfa Aesar), dimethylformamide (DMF, 99.8%, Innochem), anhydrous magnesium sulfate (AR, Fuchen), sodium chloride (AR, Fuchen), potassium carbonate (99%, Fuchen), anhydrous dichloromethane (DCM, 99.9%, J&K Scientific), anhydrous tetrahydrofuran (THF, 99.9%, Innochem), dicyclohexylcarbodiimide (DCC, 99%, Innochem), N,N-dimethylpyridin-4-amine 4methylbenzenesulfonate (DPTS, 97%, Alfa Aesar), and 2,2'-azobis(2methylpropionitrile) (AIBN, 99%, Macklin). 1,4-Dioxane (AR, Damao) was dried over CaH₂ and distilled before use. Methyl acrylate (MA, 99.0%, Macklin) and 2-(dimethylamino)ethyl methacrylate (DMAEMA, 99%, Macklin) were passed through a short basic Al₂O₃ column to remove the radical inhibitor before use. 4-Cyano-4-(dodecylsulfanylthiocarbonyl)sulfanylpentanoic acid (CDPA) was synthesized following procedures reported in our previous work.4



TPE-40EtOH

Synthesis of 2,2',2",2"'-((Ethene-1,1,2,2-tetrayltetrakis(benzene-4,1-diyl))tetrakis(oxy))tetrakis(ethan-1-ol) (TPE-4OEtOH). Compound TPE-4OEtOH was synthesized by a transesterification reaction. TPE-4OH (2.97 g, 7.5 mmol, 1 equiv) was dissolved in DMF (150 mL). Potassium carbonate (0.41 g, 3.0 mmol, 0.4 equiv) and ethylene carbonate (2.91 g, 33.0 mmol, 4.4 equiv) were added, and the reaction mixture was refluxed at 120 °C for 6 h, cooled to room temperature, poured into water (500 mL), and extracted with EA (100 mL \times 4). The combined organic phase was washed with water (100 mL \times 3) and brine (100 mL), dried over anhydrous MgSO₄, filtered, and evaporated under a vacuum. The crude product was recrystallized from acetone/petroleum ether (6/1), yielding TPE-4OEtOH as light brown needle-like crystals, $R_f = 0.11$ (acetone/nhexane = 5/4). Product: 3.18 g. Yield: 74%. ¹H NMR (400 MHz, DMSO- d_6): δ 6.84 (d, J = 8.8 Hz, 8H, ArH, 2,6 positions), 6.69 (d, J= 8.8 Hz, 8H, ArH, 3,5 positions), 4.82 (t, J = 5.5 Hz, 4H, OH), 3.90 $(t, J = 4.9 \text{ Hz}, 8H, \text{ArOCH}_2), 3.67 \text{ (td}, J = 4.9, 5.5 \text{ Hz}, 8H,$ ArOCH₂CH₂). ¹³C NMR (151 MHz, DMSO-d₆): δ 156.93, 137.98, 136.23, 132.02, 113.69, 69.31, 59.60. ESI-MS m/z of $[M + H]^+$ calculated for C34H36O8: 573.2488; found: 573.2486.



Synthesis of TPE-1Br-3OH, TPE-2Br-2OH, and TPE-3Br-1OH. TPE-1Br-3OH, TPE-2Br-2OH, and TPE-3Br-1OH were synthesized by the esterification reaction of TPE-4OEtOH with 2-bromopropionyl bromide in one pot. Under N2 protection, 2-bromopropionyl bromide (0.57 mL, 5.42 mmol, 2 equiv) was added dropwise to a THF solution (45 mL) of TPE-4OEtOH (1.56 g, 2.71 mmol, 1 equiv) and triethylamine (1.51 mL, 10.84 mmol, 4 equiv) under vigorous agitation at 0 °C. After that, the reaction was allowed to warm to 25 °C and react for 3 h. Then, the reaction mixture was filtered to remove triethylamine hydrochloride and evaporated under a vacuum. Column chromatography using gradient elution (acetone/n-hexane = 1/6 to 2/1) gave the following: TPE-1Br-3OH as a light yellow solid, $R_{\rm f} = 0.27$ (acetone/*n*-hexane = 5/4). Product: 0.54 g. Yield: 28%; TPE-2Br-2OH as a light yellow oil, $R_f = 0.48$, 0.54, and 0.61 (acetone/n-hexane = 5/4). Product: 0.60 g. Yield: 26%; and TPE-3Br-1OH as a light yellow oil, $R_f = 0.75$ (acetone/*n*-hexane = 5/4). Product: 0.49 g. Yield: 19%.



TPE-1Br-3OH

TPE-1Br-3OH. ¹H NMR (400 MHz, CDCl₃): δ 6.92 (d, J = 8.7 Hz, 8H, ArH, 2,6 positions), 6.65 (d, J = 8.7 Hz, 8H, ArH, 3,5 positions), 4.52–4.44 (m, 2H, C(=O)OCH₂), 4.40 (q, J = 6.9 Hz, 1H, CHBr), 4.14 (t, J = 4.9 Hz, 2H, C(=O)OCH₂CH₂), 4.04–3.98 (m, 6H, CH₂CH₂OH), 3.92 (m, 6H, CH₂OH), 2.12 (br, 3H, OH), 1.83 (d, J = 6.9 Hz, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 170.42, 157.02, 156.75, 138.64, 138.51, 137.46, 137.25, 132.70, 113.95, 113.82, 69.09, 65.48, 64.34, 61.57, 39.85, 21.73. ESI-MS m/z of [M + H]⁺ calculated for C₃₇H₃₉BrO₉: 709.1843; found: 709.1847.



TPE-2Br-2OH

TPE-2Br-2OH. ¹H NMR (400 MHz, CDCl₃): δ 6.92 (d, J = 8.8 Hz, 8H, ArH, 2,6 positions), 6.65 (d, J = 8.8 Hz, 8H, ArH, 3,5 positions), 4.48 (m, 4H, C(=O)OCH₂), 4.40 (q, J = 6.9 Hz, 2H, CHBr), 4.14 (t, J = 4.7 Hz, 4H, C(=O)OCH₂CH₂), 4.05–3.98 (m, 4H, CH₂CH₂OH), 3.92 (m, 4H, CH₂OH), 2.08 (br, 2H, OH), 1.83 (d, J = 6.9 Hz, 6H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 170.41, 157.04, 156.76, 138.58, 137.44, 137.23, 132.70, 113.96, 113.82, 69.09, 65.49, 64.34, 61.59, 39.85, 21.73. ESI-MS m/z of [M + H]⁺ calculated for C₄₀H₄₂Br₂O₁₀: 843.1202; found: 843.1196.



TPE-3Br-1OH

TPE-3Br-1OH. ¹H NMR (400 MHz, CDCl₃): δ 6.92 (d, J = 8.7 Hz, 8H, ArH, 2,6 positions), 6.65 (d, J = 8.7 Hz, 8H, ArH, 3,5 positions), 4.48 (m, 6H, C(=O)OCH₂), 4.40 (q, J = 6.9 Hz, 3H, CHBr), 4.14 (t, J = 4.6 Hz, 6H, C(=O)OCH₂CH₂), 4.05–4.00 (m, 2H, CH₂CH₂OH), 3.93 (m, 2H, CH₂OH), 2.03 (t, J = 5.9 Hz, 1H,

OH), 1.83 (d, *J* = 6.9 Hz, 9H, CH₃). ¹³C NMR (151 MHz, CDCl₃): δ 170.40, 157.05, 156.79, 138.65, 138.53, 137.42, 137.21, 132.70, 113.95, 113.82, 69.08, 65.49, 64.34, 61.61, 39.85, 21.74. ESI-MS *m*/*z* of [M + H]⁺ calculated for C₄₃H₄₅Br₃O₁₁: 977.0570; found: 977.0566.

Typical Procedure for the Cu(0)-Catalyzed SET-LRP of MA. To a 10 mL Schlenk tube were added MA (11.1 mmol, 1.0 mL), DMSO (0.5 mL, containing 0.005 mmol of Me₆-TREN), and initiator (TPE-*n*Br-(4-*n*)OH, n = 1-3, 0.05 mmol). The reaction mixture was subjected to deoxygenation by six freeze-pump-thaw cycles. Then, the Schlenk tube was opened under a positive flow of N2 to add a stir bar wrapped with a Cu(0) wire of 12.5 cm in length. Two additional freeze-pump-thaw cycles were carried out while holding the stir bar above the reaction mixture using an external magnet. Following that, the Schlenk tube was backfilled with N2 and placed in a water bath at 25 °C. Subsequently, the stir bar was dropped gently into the reaction mixture, which defined t = 0. For kinetic analysis, aliquots were withdrawn at different intervals with a deoxygenated syringe and a stainless steel needle after purging the side arm of the Schlenk tube with N₂ for 2 min. The withdrawn samples were dissolved in CDCl₃, quenched by bubbling with air, and subjected to ¹H NMR spectroscopy to determine monomer conversions. To obtain the molecular weight and polydispersity index (D), the samples were dried under a vacuum to remove the solvent and residual monomer, dissolved in THF, passed through a short basic Al₂O₃ column to remove residual copper, and analyzed by GPC. The yielded PMA solutions were precipitated in cold methanol three times and dried under a vacuum until a constant weight was attained.

Typical Procedure for the Esterification Reaction of TPE-(PMA)_n-(4-n)OH with CDPA. To a 25 mL pressure-resistant bottle were added TPE-(PMA)_n-(4-n)OH (0.13 mmol), CDPA (5 equiv with respect to hydroxyl groups), DCC (5 equiv with respect to hydroxyl groups), DPTS (0.5 equiv with respect to hydroxyl groups), and anhydrous DCM (12 mL). The reaction mixture was deoxygenated by purging with N₂ for 5 min. Subsequently, the Schlenk tube was placed in an oil bath at 40 °C and stirred for 48 h. Then, the resulting TPE-(PMA)_n-(4-n)CDPA was precipitated in cold methanol three times and dried under a vacuum until a constant weight was reached.

Typical Procedure for the RAFT Polymerization of DMAEMA. DMAEMA (0.3144 g, 2 mmol), TPE-(PMA)_n-(4-n)CDPA (0.01 mmol), AIBN (0.2 equiv with respect to CDPA), and 1,4-dioxane were added into a 10 mL Schlenk tube. The resulting mixture was deoxygenated by three freeze–pump–thaw cycles and backfilled with N₂. Then, the Schlenk tube was placed in an oil bath at 65 °C and heated for 8 h. After polymerization, a sample was withdrawn from the Schlenk tube, dissolved in CDCl₃, quenched by bubbling with air, and subjected to ¹H NMR spectroscopy to determine monomer conversion. The yielded TPE-(PMA)_n-(PDMAEMA)_{4-n} was precipitated into excessive *n*-hexane four times (from 1.5 mL of THF) and dried under a vacuum until a constant weight was reached.

Characterization. Nuclear magnetic resonance (NMR) experiments were conducted with a Bruker spectrometer (400/600 MHz, Bruker, Germany) at room temperature with tetramethylsilane as the internal standard and CDCl₃/(CD₃)₂SO as the deuterated solvent. For variable-temperature experiments, the miktoarm star polymer at a concentration of 25 mg/mL was tested in an EtOH- d_6/D_2O (40/60 v/v) mixture in the temperature range of 25–55 °C. A gel permeation chromatograph (GPC, Agilent 1260 Infinity II, Agilent, US) was used to determine the number-average molecular weight (M_n) , weightaverage molecular weight (M_W) , and D of TPE-(PMA)_n-(4-n)OH (n = 1-3) using polystyrene (PS770-PS1350000, Agilent Technologies) as the standard. The instrument was equipped with two Agilent gel columns (MIXED-C 300 × 7.5 mm), a G7162A refractive index detector, and a G7129A vial sampler. THF (HPLC grade, CNW) was used as the eluent at a flow rate of 1 mL/min. The GPC analysis of TPE-(PMA)_n-(PDMAEMA)_{4-n} (n = 1-3) was performed with a Waters E2695 GPC instrument (US) at 50 °C with dimethylformamide (DMF)/lithium bromide (LiBr, 1.6 g/L) as eluent (1 mL/min). The instrument was equipped with Polargel-M columns and a 2414

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Scheme 1. Synthesis of TPE-*n*Br-(4-*n*)OH $(n = 1-3)^{a}$



"Reagents and conditions: (i) ethylene carbonate, K₂CO₃, DMF, reflux, 120 °C, 6 h; (ii) 2-bromo-2-methylpropanoyl bromide, Et₃N, anhydrous THF, 0–25 °C, 3 h, stirring.

refractive index detector. Poly(methyl methacrylate) standards were used for calibration. Transmission electron microscopy (TEM) imaging was performed on a transmission electron microscope (HT7700, Hitachi, Japan) operating at an accelerating voltage of 120 kV. Samples were dropped onto copper grids, and the solvent was removed with filter paper after 3 min. Subsequently, the sample was negatively stained with uranium acetate (0.1 wt %). After 20 s, excess negative staining solution was removed using filter paper. The m/zvalues of the AIE-active initiators were obtained with a liquid chromatography-tandem mass spectrometry instrument (LC-MS, Xevo G2 QTof, Waters, US). Fourier transform infrared (FTIR) analysis was conducted on an infrared spectrometer (Nicolet Nexus 670, Thermo, US), and the samples were prepared using the potassium bromide (KBr) pellet method. A photoluminescence spectrometer (FS5, Edinburgh, UK) was utilized to record fluorescence spectra, determine the absolute fluorescence quantum yields (Φ) , and monitor the change in the fluorescence intensity of polymer samples in H₂O/EtOH mixture with temperature. Variabletemperature dynamic laser scattering (DLS, Z90, Marven, UK) was used to characterize the hydrodynamic size of polymer samples in a H₂O/EtOH mixture at different temperatures. Ultraviolet-visible (UV-vis) spectroscopy of samples was conducted with a Shimadzu UV-2600i UV-vis spectrophotometer (Japan).

RESULTS AND DISCUSSION

Synthesis of the AIE-Active Multifunctional SET-LRP Initiators. As illustrated in Scheme 1, the synthesis of the AIEactive mono/di/trifunctional SET-LRP initiators was performed in two steps: (1) the synthesis of TPE-4OEtOH by the transesterification reaction of TPE-4OH with ethylene carbonate and (2) the esterification of the hydroxyl groups of TPE-4OEtOH with a substoichiometric amount of 2bromopropionyl bromide. In the second step, TPE-3Br-1OH, TPE-2Br-2OH, and TPE-1Br-3OH were formed in one pot. Due to the wide polarity gaps among the three target molecules, they can be separated and purified facilely by column chromatography using gradient elution (acetone/nhexane = 1/6 to 2/1). The molar ratio of 2-bromopropionyl bromide/OH and the method of mixing reactants were optimized to attain the most favorable product distribution. By adding diluted 2-bromopropionyl bromide/THF solution (containing 0.5 equiv of 2-bromopropionyl bromide with respect to OH) dropwise into vigorously stirred TPE-4EtOH/ THF solution, TPE-1Br-3OH, TPE-2Br-2OH, and TPE-3Br-1OH can be obtained in 28, 26, and 19% yields, respectively (overall yield: 73%). This synthetic strategy reduces the synthetic challenges greatly and avoids the otherwise tedious and laborious procedures. A similar strategy has also been reported by Tomokazu et al.⁵⁴ in the synthesis of heterofunctionalized siloxane core units [(CH=CH₂)₃-core- $(OH)_1$, $(CH=CH_2)_2$ -core- $(OH)_2$, and $(CH=CH_2)$ -core- $(OH)_{3}].$

The chemical structures of TPE-4OEtOH, TPE-1Br-3OH, TPE-2Br-2OH, and TPE-3Br-1OH were confirmed by ¹H NMR, ¹³C NMR, FTIR, and ESI-MS (Experimental Section and Figures S1–S3). The characteristic ¹H NMR signals from methyl and methine protons of the bromopropionate moieties peaked at ~1.83 and 4.40 ppm, respectively (Figure 1). Compared with TPE-4EtOH, the FTIR spectra of TPE-*n*Br-(4-*n*)OH (n = 1-3) display two new peaks at 1740 and 679 cm⁻¹, corresponding to the C=O stretching vibration band of the ester group and the C–Br stretching vibration band,



Figure 1. ¹H NMR spectra of (a) TPE-4OEtOH, (b) TPE-1Br-3OH, (c) TPE-2Br-2OH, and (d) TPE-3Br-1OH in $(CD_3)_2$ SO/CDCl₃. ¹H NMR resonances from residual solvent in $(CD_3)_2$ SO/CDCl₃ are indicated by an asterisk (*).

respectively (Figure S2). The intensity of both peaks increases with the increasing functionality of TPE-nBr-(4-n)OH.

Synthesis of TPE-(PMA)_n-(4-*n*)OH and TPE-(PMA)_n-(4-*n*)CDPA (n = 1-3). As depicted in Scheme 2, the SET-LRP of MA initiated from TPE-*n*Br-(4-*n*)OH (n = 1-3) produces AIE-active PMA that is linear with TPE at one chain-end for n = 1, linear with TPE at the midchain position for n = 2, and three-arm star with TPE at the core for n = 3. The SET-LRP kinetics of MA in DMSO ($[MA]_0/[TPE-nBr-(4-n)OH]_0/[Me_6-TREN] = 222/1/0.1$) was first studied, and representative results are shown in Figure 2. In all cases, polymerization proceeded quickly and achieved over 78% conversion within 17 min. A linear relationship of $\ln[M]_0/[M]$ with time was obtained, suggesting that the concentrations of chain radicals remained unchanged during all polymerizations. The apparent propagation rate constants (k_p^{app}) derived from the slopes of

the kinetic plots were in the following order: TPE-1Br-3OH $(0.081 \text{ min}^{-1}) < \text{TPE-2Br-2OH} (0.096 \text{ min}^{-1}) < \text{TPE-3Br-}$ 10H (0.103 min⁻¹). A similar trend showing accelerated polymerization with increasing initiator functionality at a fixed $[MA]_0/[initiator]_0$ has also been reported by Percec's group⁵⁵ and in our previous work.⁴⁵ $M_{n,GPC}$ increased linearly with increasing MA conversion and agreed well with $M_{n,th}$ (calculated by $MW_{initiator} + MW_{MA} \times Conv._{MA} \times [MA]_0/$ $[TPE-nBr-(4-n)OH]_0$ while assuming 100% initiator efficiency. The absence of obvious tailing in GPC traces (Figure S4) and the gradual reduction of D to approximately 1.15 indicated that the SET-LRP of MA was well controlled. The ¹H NMR and GPC results of TPE-(PMA)_n-(4-n)OH synthesized at different [MA]₀/[TPE-nBr-(4-n)OH]₀ values are given in Figures S5 and S6 and summarized in Table 1. Therefore, well-defined TPE- $(PMA)_n$ -(4-n)OH homopolyScheme 2. Synthesis of TPE-(PMA)_n-(4-n)OH and TPE-(PMA)_n-(4-n)CDPA (n = 1-3) Cu(0) wire / Me₆-TREN, DCC. DPTS, anhydrous DMSO, 25 °C, 16 h DCM, 40 °C, 48 h TPE-1Br-3OH TPE-PMA-3OH TPE-PMA-3CDPA NC/5H2,C12H26 () Cu(0) wire / Me₆-TREN, DCC, DPTS, anhydrous DMSO, 25 °C, 16 h DCM, 40 °C, 48 h TPE-(PMA)2-2CDPA TPE-(PMA)₂-2OH TPE-2Br-2OH ^{NC}∕s^µs^{,C}1₂H₂ (1 Cu(0) wire / Me6-TREN, DCC, DPTS, anhydrous DMSO, 25 °C, 16 h DCM, 40 °C, 48 h TPE-(PMA)₃-10H TPE-(PMA)₃-1CDPA TPE-3Br-10H

mers with one to three PMA arms were obtained successfully (see Figure S7 for GPC traces).

After their successful synthesis, TPE-(PMA)_n-(4-n)OH were subjected to the Steglich esterification reaction with CDPA in the presence of DCC and DPTS in DCM (Scheme 2). ¹H NMR spectra of the obtained TPE-(PMA)_n-(4-n)CDPA demonstrate good agreement of the integral ratios of characteristic protons with theoretical values while assuming 100% conversion of the hydroxyl groups (Figure 3). Besides, the NMR absorptions of methylene protons ($-OCH_2CH_2OH$) at 4.01 and 3.92 ppm disappear completely. GPC results show no obvious change in M_n after the Steglich esterification reaction (Table S1). Therefore, the quantitative introduction of the CDPA moiety was accomplished, yielding TPE-(PMA)_n-(4-n)CDPA that enabled a mechanistic transition to RAFT polymerization.

Synthesis of Miktoarm Star TPE-(PMA)_n-(PDMAE-MA)_{4-n} (n = 1-3). TPE-(PMA)_n-(4-n)CDPA were used as macro-chain transfer agents (macro-CTA) in the RAFT polymerization of DMAEMA at a fixed ratio of [TPE-(PMA)_n-(4-n)CDPA]/[AIBN] = 5/1 at 65 °C for 8 h. As shown in Scheme 3, this produces miktoarm star polymers with a TPE core and different PMA/PDMAEMA arm numbers, which are denoted as TPE-(PMA)_n-(PDMAE-MA)_{4-n} (n = 1-3). $M_{n,NMR}$, derived from the integral ratios of characteristic protons (see Figure 4), are in good consistence with $M_{n,th}$ (calculated by MW_{macro-CTA} + MW_{DMAEMA} × Conv._{DMAEMA} × [DMAEMA]₀/[macro-CTA]₀) and $M_{n,GPC}$ obtained with DMF-phase GPC (Table 2). The distribution of GPC traces (Figure S8) and moderate \mathcal{D} (<1.45) indicate acceptable control over the RAFT polymerization without serious star—star coupling reactions. Therefore, the precise synthesis of miktoarm star TPE- $(PMA)_{n}$ - $(PDMAEMA)_{4-n}$ was accomplished successfully, providing an opportunity to gain fundamental insight into the thermoresponsive behavior—macromolecular architecture correlation.

Macromolecular Architecture-Correlated UCST and Fluorescence Behavior of TPE-(PMA)_n-(4-n)OH (n = 1-3). Prior to the investigation of the miktoarm star polymers, it is important to evaluate the thermoresponsiveness and accompanying photoluminescence (PL) behavior of TPE- $(PMA)_{n}$ -(4-n)OH homopolymers. We first carried out turbidimetry at [TPE] = 100 μ M in EtOH/H₂O mixtures (volume fraction Φ_{EtOH} = 100, 80, and 60%), showing a typical reversible UCST behavior with a small hysteresis (1-3 $^{\circ}C$ difference in cloud points $T_{\rm cp}$ between heating and cooling) in all cases (Figure S9). As Φ_{EtOH} was decreased from 100 to 80%, significant reductions in T_{cp} from approximately 65–69 to 11-18 °C were observed (Table S2). Such cosolvency effect in EtOH/H2O mixtures has been reported for poly(methyl methacrylate) (PMMA)⁵⁶ and PMA.⁵⁷ This has been attributed to the existence of the majority of water molecules in single, nonclustered state within the corresponding concentration regime, which facilitates water-polymer hydrogen bonding and promotes the enthalpy-driven solvation process of polymers.⁵⁸ A further reduction of $\Phi_{\rm EtOH}$ to 60% caused T_{cp} to rebound (26–32 °C), suggesting that the reformation of large water clusters aggravated water-polymer hydrogen bonding and decreased the solubility of TPE- $(PMA)_n$ -(4-*n*)OH homopolymers. When Φ_{EtOH} was decreased beyond 40%, $T_{\rm cp}$ exceeded the boiling point of the EtOH/H2O



Figure 2. Monomer conversion, kinetic plots, and evolution of $M_{n,GPC}$ and $\mathcal{D}(M_w/M_n)$ for the SET-LRP of MA in DMSO initiated from (a) TPE-1Br-3OH, (b) TPE-2Br-2OH, and (c) TPE-3Br-1OH and catalyzed by the 12.5 cm nonactivated Cu(0) wire at 25 °C. Reaction conditions: MA = 1 mL, DMSO = 0.5 mL, and $[MA]_0/[initiator]_0/[Me_6-TREN]_0 = 222/1/0.1$.

Table 1. Results of the SET-LRP of MA Initiated from TPE-*n*Br-(4-n)OH (n = 1-3)

| | conv. % ^a | $M_{ m n,th}{}^{b}$ | DP ^c | $M_{\rm n,NMR}^{d}$ | $M_{ m n,GPC}^{e}$ | Đ |
|---|----------------------|---------------------|-----------------|---------------------|--------------------|------|
| TPE-PMA ₂₂₂ -3OH | 98 | 19,400 | 222 | 19,800 | 23,800 | 1.13 |
| TPE-(PMA ₁₀₈) ₂ -2OH | 97 | 19,400 | 216 | 19,400 | 22,200 | 1.16 |
| TPE-(PMA ₇₃) ₃ -1OH | 96 | 19,300 | 220 | 19,900 | 21,900 | 1.17 |
| TPE-PMA ₅₆ -3OH | 99 | 5400 | 56 | 5500 | 6500 | 1.22 |
| TPE-(PMA ₂₈) ₂ -2OH | 99 | 5500 | 56 | 5700 | 5400 | 1.15 |
| TPE-(PMA ₂₈) ₃ -1OH | 99 | 7800 | 84 | 8200 | 8400 | 1.19 |
| | | | | | | |

^{*a*}Measured by ¹H NMR. ^{*b*}Theoretical M_n calculated by MA conversion. ^{*c*}DP calculated by the peak area ratios of the methyl protons of PMA and the aromatic protons of TPE-*n*Br-(4-*n*)OH given by ¹H NMR. ^{*d*} M_n calculated by ¹H NMR. ^{*c*} M_n measured by GPC. Polymerization conditions: 12.5 cm of Cu(0) wire (1 mm in diameter), 25 °C, 1 mL of MA in 0.5 mL of DMSO, and [TPE-nBr-(4-*n*)OH]/[Me₆-TREN] = 1/0.1.

mixtures. The trend of $T_{\rm cP}$ with $\Phi_{\rm EtOH}$ agrees well with the case reported by Can et al.,⁵⁷ but the corresponding $T_{\rm cP}$ values at identical $\Phi_{\rm EtOH}$ are different to some extent. This may be attributed to the altered solubility of PMA because of the introduction of the TPE moiety, the higher chain length, and the miktoarm star topology of TPE-(PMA)_n-(4-n)OH in the present work.

The number of PMA chains attached to the TPE moiety brought about slight changes in the turbidity-temperature plots. As summarized in Table S2 and Figure S10, increasing *n* from 1 to 3 resulted in a small elevation of $T_{\rm cp}$ by 3–4 °C and a slight broadening of the phase transition temperature range. This implies that more PMA chains around the TPE moiety can hinder the insoluble-to-soluble transition during heating,⁵⁹ although the underlying mechanism still needs to be revealed.

After the confirmation of UCST behavior, we are curious to know if the integration of the TPE group with UCST polymer PMA can deliver a thermoresponsive AIE behavior. As shown

in Figure 5 and Figure S11, the emission of $TPE-(PMA)_n-(4$ *n*)OH was intensive at -20 °C, originating from the restricted intramolecular motion (RIM) of the TPE group 60,61 by surrounding PMA chains in an undissolved state. With increasing temperature, the fluorescence intensity first decreased slowly at low temperature, then underwent a linear response range, and finally plateaued with almost negligible emission. This was accompanied by the transition of large TPE- $(PMA)_n$ -(4-n)OH aggregates into unimer/very small molecular aggregates upon heating (see Figures S12 and S13). It is notable that the fluorescence linear response range spanned over a much broader temperature range (18–48 °C) than the phase transition range obtained by turbidimetry (3-10 °C). This obvious inconsistency is because fluorescence responsiveness is closely related to a change in the mobility of AIEgen, whereas the phase transition observed by UV-vis spectroscopy corresponds to the formation/disappearance of large intermolecular aggregates.⁶²



Figure 3. ¹H NMR spectra of (a) TPE-PMA₂₂₂-3CDPA, (b) TPE-(PMA₁₀₈)₂-2CDPA, and (c) TPE-(PMA₇₃)₃-1CDPA in CDCl₃. ¹H NMR resonances from the residual solvent in CDCl₃ are indicated by an asterisk (*). The ratios on the top right are theoretical values obtained by assuming 100% conversion of the hydroxyl groups of TPE-(PMA)_n-(4-n)OH.

It is remarkable that the number of PMA chains attached to TPE-(PMA)_n-(4-n)OH had a profound effect on the linear temperature range and the fluorescence dynamic range. For instance, increasing *n* from 1 to 3 at Φ_{EtOH} = 60% shifted the linear temperature range rightward, which were -2.3-27.8, 0-28.6, and 7.6-34.5 °C, respectively. This agrees well with the trend of the phase transition range determined by turbidimetry. Strikingly, more PMA chains brought about more intensive fluorescence at identical temperature, which can be ascribed to the worsened solvation, more sterically hindered microenvironment of the TPE moiety, and thus more effective blocking of nonradiative decay. A similar behavior has been reported by us⁴⁵ and other researchers.⁶³ For n = 1, 2, and 3,the I/I_0 values (defined as the ratio of peak PL intensity at -20and 40 °C) were 87.0, 60.1, and 36.7 for $\Phi_{\rm EtOH}$ = 60%, respectively (Figure S14). The $EtOH/H_2O$ composition provides another handle for tuning the thermoresponsive PL

behavior of TPE-(PMA)_n-(4-*n*)OH. At $\Phi_{EtOH} = 100\%$, the fluorescence linear response of TPE-(PMA₇₃)₃-1OH occurred at -1.9-46.5 °C, covering the biologically meaningful temperature range. The highly tunable thermoresponsive PL behavior of TPE-(PMA)_n-(4-*n*)OH by altering the macromolecular architecture and EtOH/H₂O composition indicates its great potential as a fluorescent thermometer.

Macromolecular Architecture-Correlated UCST and Fluorescence Behavior of TPE-(PMA)_{*n*}-(**PDMAEMA**)_{*4-n*} (*n* = 1–3). Encouraged by the interesting behavior of TPE-(PMA)_{*n*}-(4-*n*)OH, we investigated the thermoresponsiveness and fluorescence behavior of miktoarm star TPE-(PMA)_{*n*}-(PDMAEMA)_{*4-n*}, aiming to reveal their correlation with the macromolecular architecture. It should be noted here that both PMA and PDMAEMA can be thermoresponsive in EtOH/ H_2O mixtures, displaying UCST and LCST behavior, respectively. Therefore, the integration of PMA and Scheme 3. Synthesis of TPE-(PMA)_n-(PDMAEMA)_{4-n} (n = 1-3)



PDMAEMA in the miktoarm star TPE-(PMA)_n-(PDMAE- $MA)_{4-n}$ may lead to different thermoresponse modes with increasing temperature: (1) only UCST, (2) UCST followed by LCST, (3) LCST followed by UCST, and (4) only LCST. $\Phi_{
m EtOH}$ was decreased to 60, 40, and 20% because higher $\Phi_{
m EtOH}$ would lead to the UCST of PMA being too low to be detected by variable-temperature UV-vis spectroscopy. Intriguingly, the EtOH/H₂O dispersions of TPE-(PMA)_n-(PDMAEMA)_{4-n} displayed >90% transmittance at low temperature and did not show a sharp turbidity change (Figure 6a-c) as in the cases of TPE-(PMA)_n-(4-n)OH homopolymers (Figure S9). Probably, the solvophilic PDMAEMA played the role of stabilizing arm for insoluble PMA at low temperature and promoted the formation of small stabilized micellar aggregates rather than large aggregates that can scatter light intensively.⁶² Thus, turbidimetry was incapable of probing the UCST phase transition process at the investigated polymer concentration $(\sim 4.8 \text{ mg/L}).$

Despite the absence of a typical turbidity change in UCST, variable-temperature fluorescence spectroscopy displayed remarkable thermoresponsiveness for TPE-(PMA)_n-(PDMAE-MA)_{4-n} at [TPE] = 100 μ M. Representative results are presented in Figure 6 and Figure S15. The peak fluorescence intensity (at 440–475 nm) descended with increasing temperature for all miktoarm star polymers, which resembled the case of TPE-(PMA)_n-(4-n)OH homopolymers. Nevertheless, the attachment of one to three PDMAEMA arms led to fascinating changes in the following aspects:

1) The peak PL intensity of TPE- $(PMA)_n$ - $(PDMAE-MA)_{4-n}$ decreased significantly (especially at low temperature) compared with the corresponding value of TPE- $(PMA)_n$ -(4-n)OH at identical *n*. This indicates

that the attachment of solvophilic PDMAEMA arm/ arms to the TPE core can aid its solvation in the EtOH/ $\rm H_2O$ mixture through enhanced polymer–solvent interactions. Therefore, the higher mobility of TPE group can be achieved, leading to weakened emission according to the RIM mechanism.

2) At low temperature, TPE-(PMA₇₃)₃-PDMAEMA₁₇₈ displayed remarkably higher PL intensity than the other two miktoarm star polymers. Meanwhile, the absolute fluorescence quantum yields (Φ) of TPE- $(PMA_{73})_3$ -PDMAEMA₁₇₈ in EtOH/H₂O mixtures with $\Phi_{\rm EtOH} = 60\%$ (14.69%), 40% (20.52%), and 20% (34.36%) at 25 °C were all much higher than the corresponding values of the other miktoarm star polymers (Figure S16), indicating that the combination of three PMA arms and one PDMAEMA arm conferred a much higher level of RIM on the TPE group than the other combinations. Owing to the accompanied effect of different macromolecular architecture on the PL intensity at high temperature, the I/I_0 (defined as the ratio of peak PL intensity at -20 and 70 °C) did not always increase monotonically with increasing n for TPE-(PMA)_n-(PDMAEMA)_{4-n} at different Φ_{EtOH} . As shown in Figure S17, the I/I_0 values at $\Phi_{\rm EtOH}$ = 60% for TPE-PMA₂₂₂-(PDMAEMA₅₉)₃, TPE-(PMA₁₀₈)₂-(PDMAEMA₈₉)₂, and TPE-(PMA₇₃)₃-PDMAEMA₁₇₈ were 40.4, 18.6, and 69.9, respectively. The dynamic range of TPE-(PMA)_n-(PDMAEMA)_{4-n} in the present work is significantly higher than those of the four-arm star polymer TPE-tetraPDEAEAM (3),⁶⁴ AIEgen-grafted copolymer P(NIPAM-*co*-EM) (4),⁴ and the AIE-active core cross-linked multimiktoarm star copoly-



Figure 4. ¹H NMR spectra of (a) TPE-PMA₂₂₂-(PDMAEMA₅₉)₃, (b) TPE-(PMA₁₀₈)₂-(PDMAEMA₈₉)₂, and (c) TPE-(PMA₇₃)₃-PDMAEMA₁₇₈ in CDCl₃. ¹H NMR resonances from the residual solvent in CDCl₃ are indicated by an asterisk (*). Polymerization conditions: [DMAEMA]/[TPE-(PMA)_n-(4-n)CDPA]/[AIBN] = 200/1/0.2, 65 °C, and 8 h.

| Table 2. Characterization Results of TPE-(PMA) _n -(PDMAEMA) _{4-n} ($n =$ | 1 - 3 | 3 |
|---|-------|---|
|---|-------|---|

| | conv. % ^a | $M_{ m n,th}{}^{b}$ | DP ^c | $M_{ m n,NMR}^{d}$ | $M_{ m n,GPC}^{e}$ | Ð |
|---|----------------------|---------------------|-----------------|--------------------|--------------------|------|
| TPE-PMA ₂₂₂ -(PDMAEMA ₅₉) ₃ | 90 | 48,900 | 177 | 48,800 | 49,800 | 1.23 |
| $TPE-(PMA_{108})_2-(PDMAEMA_{89})_2$ | 87 | 47,600 | 178 | 48,200 | 42,700 | 1.32 |
| TPE-(PMA ₇₃) ₃ -PDMAEMA ₁₇₈ | 91 | 48,300 | 178 | 48,300 | 50,500 | 1.45 |
| TPE-PMA ₂₂₂ -(PDMAEMA ₄₄) ₃ | 72 | 43,200 | 132 | 41,400 | 43,600 | 1.21 |
| $TPE-(PMA_{111})_2-(PDMAEMA_{65})_2$ | 80 | 45,200 | 130 | 40,600 | 43,100 | 1.27 |
| TPE-(PMA ₇₄) ₃ -PDMAEMA ₁₄₀ | 78 | 44,200 | 140 | 41,700 | 44100 | 1.25 |

^{*a*}Measured by ¹H NMR. ^{*b*}Theoretical M_n calculated by DMAEMA conversion. ^{*c*}DP calculated by the peak area ratios of the methyl protons of PDMAEMA and the aromatic protons of TPE-(PMA)_n-(4-*n*)CDPA given by ¹H NMR. ^{*d*}Calculated by ¹H NMR. ^{*e*}Measured by GPC with DMF/ LiBr as eluent. Polymerization conditions: [TPE-nBr-(4-*n*)CDPA]/[AIBN] = 5/1, 65 °C, and 8 h.

mers with PE and PMAA arms (3).⁴² Thus, highly tunable temperature-responsive fluorescence properties can be achieved by endowing miktoarm star polymers

with a TPE core and different polymer arm combinations. This is anticipated to dictate vastly different mobility for the TPE core and different solvation



Figure 5. Plots of peak photoluminescence (PL) intensity of TPE-(PMA)_n-(4-*n*)OH versus temperature in EtOH/H₂O mixtures with Φ_{EtOH} values of (a) 60, (b) 80, and (c) 100%. [TPE] = 20 μ M, excitation wavelength (λ_{ex}): 320 nm. (d) Digital photographs of TPE-PMA₂₂₂-3OH (left), TPE-(PMA₁₀₈)₂-2OH (middle), and TPE-(PMA₇₃)₃-1OH (right) in an EtOH/H₂O mixture at 10 and 40 °C (right) under daylight and 365 nm UV light. [TPE] = 100 μ M, Φ_{EtOH} = 60%.



Figure 6. Transmittance (a, b, c) and plots of peak PL intensity (d, e, f) versus temperature for TPE-(PMA)_n-(PDMAEMA)_{4-n} in EtOH/H₂O mixtures with Φ_{EtOH} being (a, d) 20%, (b, e) 40%, and (c, f) 60%. [TPE] = 100 μ M, λ_{ex} : 320 nm.

dynamics during the phase transition of PMA, which will be probed and discussed in a later section.

3) Φ_{EtOH} had a greater impact not only on PL intensity but also on the linear temperature range of TPE-(PMA)_n-(PDMAEMA)_{4-n}. As depicted in Figure S18, peak PL intensity was enhanced significantly with increasing water content (decreasing Φ_{EtOH}) within the intermediate temperature range (10–50 °C). Water is a nonsolvent for PMA; thus, more water will facilitate the aggregation and RIM of the TPE core. This is quite common for AIEgens and has been reported by many researchers in the literature.^{60,61} Surprisingly, decreasing Φ_{EtOH} can expand the linear temperature range of TPE-(PMA)_n-(PDMAEMA)_{4-n} in EtOH/H₂O mixtures. For instance, the linear temperature range of TPE-(PMA₇₃)₃-PDMAEMA₁₇₈ was 0–20.0, 4.2–39.2, and 23.5–60.0 °C for Φ_{EtOH} = 60, 40, and 20%, respectively. Therefore, by adjusting the solvent composition, we are able to achieve a fairly large linear range of thermoresponsiveness.

The cyclic stability of the thermoresponsive fluorescence of TPE-(PMA)_n-(PDMAEMA)_{4-n} with Φ_{EtOH} being 40% was evaluated at 10 and 40 °C. A minimal change in peak PL intensity occurred over the investigated six cycles (Figure 7), suggesting the excellent cyclic stability of TPE-(PMA)_n-(PDMAEMA)_{4-n}. Hence, the sensitive, wide-range adjustable, and highly stable thermoresponsive emission characteristics of miktoarm star TPE-(PMA)_n-(PDMAEMA)_{4-n} make it auspi-



Figure 7. Photoluminescence (PL) spectra of (a) TPE-PMA₂₂₂-(PDMAEMA₅₉)₃, (b) TPE-(PMA₁₀₈)₂-(PDMAEMA₈₉)₂, and (c) TPE-(PMA₇₃)₃-PDMAEMA₁₇₈ in EtOH/H₂O mixtures at 10 and 40 °C. (d–f) Cyclic stability of the thermoresponsive fluorescence of TPE-(PMA)_n-(PDMAEMA)_{4-n}. [TPE] = 100 μ M, Φ_{EtOH} = 40%, λ_{ex} : 320 nm.

cious in the development of an advanced intelligent fluorescent system.

Mechanism of the Macromolecular Architecture-Correlated Phase Transition of TPE-(PMA)_n-(PDMAE- $MA)_{4-n}$ (n = 1-3). To gain deep insights into the phase transition of TPE-(PMA)_n-(PDMAEMA)_{4-n}, variable-temperature ¹H NMR was performed in EtOH-d₆/D₂O (40/60 v/v) at a polymer concentration of ~25 mg/mL from 25 to 55 °C (Figure 8). It should be kept in mind that the phase transition in EtOH- d_6/D_2O may deviate from the case in EtOH/H₂O slightly because of the well-known isotope effect.⁶² The peaks at $\delta \sim 4.0$ ppm, assigned to the overlapping of the absorptions of protons b, c, d, and e, remained well resolved within the investigated temperature range. This indicates that the LCST of PDMAEMA did not occur because the presence of solvophilic PMA at T > UCST retarded the LCST transition of PDMAEMA, causing $T_{\rm cp}$ of PDMAEMA to be higher than 55 °C. It is remarkable that the peaks assigned to the characteristic absorptions of PMA ($\delta \sim 3.56$ ppm for methyl proton f; $\delta \sim 2.50 - 1.10$ ppm for backbone methylene, protons i and j) all became narrower and stronger dramatically upon heating. The plots of integral ratio $A_{\rm b+c+d+e}/A_{\rm f}$ against temperature are presented in Figure S19, displaying a rapid decline from 25 to 35 °C and a plateau as the temperature approached ~45 °C. The plateau $A_{\rm b+c+d+e}/A_{\rm f}$ value is about 0.56, which agrees well with the corresponding value calculated from the ¹H NMR spectra recorded in CDCl₃. Thus, the solvation of PMA occurred within a rather broad temperature range at the molecular level. Our observation is similar to the case of PMA40-b-PDEGEA200 in the EtOH/H2O mixture ($\Phi_{\rm EtOH}$ = 40%) from 18 to 63 °C, with the PMA chain segments exhibiting a solvation behavior over a wide temperature range.⁵⁷ Notably, the $A_{b+c+d+e}/A_f$ values at 25 °C decrease in the following order: TPE-(PMA₇₃)₃-PDMAEMA₁₇₈ $(\sim 3.52) > \text{TPE-}(\text{PMA}_{108})_2 - (\text{PDMAEMA}_{89})_2 (\sim 1.65) > \text{TPE-}$

 PMA_{222} -(PDMAEMA₅₉)₃ (~1.49). This implies that the insoluble-to-soluble phase transition of PMA was hampered significantly with n = 3, probably due to the steric crowding of PMA arms tethered to a joint TPE core and the resulting intensified intramolecular interactions.⁵⁹ This can be further evidenced by the changes in the characteristic aromatic proton absorptions of TPE. As shown in Figure 8, the proton signals of TPE for TPE-PMA₂₂₂-(PDMAEMA₅₉)₃ were discernible at 30 °C and kept increasing in intensity as temperature increased. In sharp contrast, the proton signals of TPE for TPE- $(PMA_{108})_2$ - $(PDMAEMA_{89})_2$ were only visible at T > 35 $^{\circ}$ C, and their intensity at 55 $^{\circ}$ C was lower than the corresponding intensity of TPE-PMA₂₂₂-(PDMAEMA₅₉)₃. It is remarkable to see that the proton signals of TPE for TPE- $(PMA_{73})_3$ -PDMAEMA₁₇₈ were only observed at T > 45 °C with extremely low intensity. These results confirm that the combination of three PMA arms and one PDMAEMA arm can generate a much higher level of RIM for TPE at low temperatures and hinder the UCST phase transition upon heating. The information revealed by variable-temperature ¹H NMR is in perfect consistence with our observations on the thermoresponsive PL behavior.

Finally, we conducted variable-temperature DLS and TEM to probe the macromolecular architecture-correlated selfassembling behavior of TPE-(PMA)_n-(PDMAEMA)_{4-n} during the insoluble-to-soluble transition of PMA. For all miktoarm star polymers, D_h values were stable at 20–40 °C, jumped to a maximum at 45 °C, and then declined to some extent at 50 °C. D_h values were much larger than the contour length of TPE-(PMA)_n-(PDMAEMA)_{4-n} (see Figure S20) and the DLS results obtained for close to molecularly dissolved TPE-(PMA)_n-(4-n)OH in EtOH/H₂O mixtures with $\Phi_{\text{EtOH}} = 60\%$ at 35 °C (see Figure S12). The evolution of the nanoassembly of TPE-(PMA)_n-(PDMAEMA)_{4-n} with increasing temperature can be interpreted as follows: At 25 °C, the miktoarm star

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Figure 8. Variable-temperature ¹H NMR spectra of (a) TPE-PMA₂₂₂-(PDMAEMA₅₉)₃, (b) TPE-(PMA₁₀₈)₂-(PDMAEMA₈₉)₂, and (c) TPE-(PMA₇₃)₃-PDMAEMA₁₇₈ recorded in EtOH- d_6/D_2O (40/60 v/v). Polymer concentration: ~ 25 mg/mL.

Scheme 4. Schematic Illustration of the Thermoresponsive PL and Self-Assembling Behavior of the Miktoarm Star Polymers with TPE-(PMA₇₃)₃-PDMAEMA₁₇₈ as an Example



polymers self-assembled into micellar aggregates or large compound micelles (LCM) instead of typical core-shell micelles. Within the LCM morphology, many solvophobic pockets containing the TPE and CDPA moieties were formed, which were stabilized and connected by solvophilic PDMAE-MA arm/arms (Scheme 4). Then, as indicated by variabletemperature ¹H NMR analysis, the good solvation state of PMA was achieved at ~45 $^{\circ}$ C, which promoted the expansion of the LCM morphology significantly. Afterward, the disintegration of the expanded LCM morphology occurs to some extent, leading to the decline in $D_{\rm h}$ at 55 °C. Nevertheless, the UCST transition of PMA at high temperature did not turn the LCM morphology into a unimer state, which can be ascribed to the retention of relatively strong intermolecular solvophobic interactions among the TPE and CDPA moieties. This resembles the case of the hydrophilic poly(DEGA)-r-(OEGA), where the hydrophobic initiator residues were bent, clustered together, and confined to a polar hydrophilic solution, forcing the telechelic polymer chains to adopt a folded conformation.⁶⁵ The DLS analysis is also supported by negative stain TEM results, which show the presence of nanoparticles containing multiple primary particles (Figure S21) at 25 °C.

Notably, variation in the macromolecular architecture of TPE-(PMA)_n-(PDMAEMA)_{4-n} was also reflected in the particle size of the nanoassemblies. As depicted in Figure S20, D_h values decreased in the following order: TPE-(PMA₇₃)₃-PDMAEMA₁₇₈ > TPE-(PMA₁₀₈)₂-(PDMAEMA₈₉)₂ > TPE-PMA₂₂₂-(PDMAEMA₅₉)₃. At 25 °C, D_h values were 68, 47, and 43 nm for TPE-(PMA₇₃)₃-PDMAEMA₁₇₈, TPE-(PMA₁₀₈)₂-(PDMAEMA₈₉)₂, and TPE-PMA₂₂₂-(PDMAEMA₈₉)₂, and TPE-PMA₂₂₂-(PDMAEMA₅₉)₃, respectively. At low temperatures, the attachment of three PMA arms and one PDMAEMA arm to the TPE core facilitated the intermolecular aggregation of TPE-(PMA₇₃)₃-PDMAEMA₁₇₈ more effectively than that of the other two miktoarm star polymers. This also contributes to the remarkably higher fluorescence intensity of TPE-(PMA₇₃)₃-PDMAEMA₁₇₈ at a low temperature observed in our work.

CONCLUSIONS

In summary, a simple route has been developed to synthesize the three AIE-active TPE-nBr-(4-n)OH (n = 1-3) initiators in

one pot for the first time. By the SET-LRP of MA initiated from TPE-nBr-(4-n)OH, the attachment of CDPA via hydroxyl groups, and the subsequent RAFT polymerization of DMAEMA, structurally well-defined, thermoresponsive AIEactive miktoarm star TPE- $(PMA)_n$ - $(PDMAEMA)_{4-n}$ with precise arm numbers have been synthesized successfully. It has been found that $TPE-(PMA)_n-(4-n)OH$ and TPE- $(PMA)_n$ - $(PDMAEMA)_{4-n}$ exhibit fascinating thermoresponsive photoluminescence behavior in EtOH/H2O mixtures originating from the UCST transition of the PMA arm. The macromolecular structure generates a remarkable contrast in the fluorescence thermoresponsiveness of different TPE- $(PMA)_n$ - $(PDMAEMA)_{4-n}$. Increasing the number of PMA arms in miktoarm star TPE-(PMA)_n-(PDMAEMA)_{4-n} leads to significantly stronger emission at low temperature and larger fluorescence dynamic range. The contrast in fluorescence output arises from the fact that the macromolecular structure determines the different aggregation state and microenvironment of the TPE group at low temperature, as well as the change in solvation dynamics with increasing temperature. Our work provides a highly efficient approach to the precise synthesis of thermoresponsive AIE-active miktoarm star polymers with well-defined macromolecular structure. The insights into the correlation between the structural parameters of miktoarm star polymers and their thermoresponsive fluorescence behavior will benefit the development of a thermoresponsive intelligent fluorescence system with good sensitivity, wide-range tenability, and high stability.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.4c02525.

NMR spectra, ESI-MS spectra, GPC traces, photoluminescence spectra, variable-temperature DLS, and TEM micrographs (PDF)

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Notes

The authors declare no competing financial interest.

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