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A novel amphiphilic AB_2 star copolymer synthesized by the combination of ring-opening metathesis polymerization and atom transfer radical polymerization

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ABSTRACT

A new amphiphilic AB_2 star copolymer was synthesized by the combination of ring-opening metathesis polymerization (ROMP) and atom transfer radical polymerization (ATRP). Two different routes (methods A and B) were employed firstly to prepare the poly(oxanorbornene)-based monotelechelic polymers as the hydrophobic arm bearing dibromo-ended group via ROMP in the presence of two different terminating agents catalyzed by first generation Grubbs catalyst. The values of capping efficiency (CE) of the polymers were determined by NMR, which were 94% and 67% for methods A and B, respectively. Then, the dibromo-ended ROMP polymers were used as the macroinitiators for ATRP of 2-(dimethylamino)ethyl methacrylate (DMAEMA) to produce two hydrophilic arms. The prepared amphiphilic AB_2 star copolymers poly(7-oxanorborn-5-ene-*exo*,*exo*-2,3-dicarboxylic acid dimethyl ester)-*block*-bis[poly(2-(dimethylamino)ethyl methacrylate)] ($PONBDM_n$-*b*-$(PDMAEMA_m)_2$) with a fixed chain length of hydrophobic PONBDM and various hydrophilic PDMAEMA chain lengths can self-assemble spontaneously in water to form polymeric micelles, which were characterized by dynamic light scattering, atom force microscopy, and transmission electron microscopy measurements.

1. Introduction

Star and miktoarm star block copolymers have aroused interest due to their unique physicochemical properties as well as their potential applications as new functional materials [1]. Over the past decades, there are numerous researches on the subject of the synthesis of star polymers, since the discovery of living anionic polymerization. For synthesis of a number of star polymers, various synthetic strategies have been developed. Generally, multifunctional initiators, multifunctional linking agents, and difunctional monomers were used in the preparation of star polymers with different arms [2]. Multifunctional initiators are compounds capable of simultaneously initiating several polymerizations to form the arms of the star polymer, while the remaining moiety composes the core of the star. For example, Hedrick [3–6] reported the synthesis of several star polymers with various arms from miktofunctional or protected initiators by using consecutive atom transfer radical polymerization (ATRP) or combination with ring-opening polymerization (ROP), and several articles [7–9] have been also published for the synthesis of the star-shaped polynorbornene by using multi-nuclear dendritic Ru-complexes as catalysts via ring-opening metathesis polymerization (ROMP). Multifunctional linking agents are compounds with several reactive sites, which can react with living chains and represent the most efficient way to synthesize well-defined star polymers due to the absolute control afforded in all the synthetic steps. Faust [10] reported a general and efficient method to synthesize triarm star homo-(A_3) and hetero-arm (A_3B_3) star copolymers by employing multifunctional living linking agents. Feast [11] prepared linear and star poly(L-pentenylene)s via ROMP by using di- and trifunctional aldehydes in the Wittig-like capping reactions of the living polymers, which initiated with a well-defined tungsten alkylidene complex. In using difunctional monomers method, an end-reactive polymer precursor is used as initiator for the polymerization of a small amount of suitable difunctional monomers. Several star polymers have been prepared by making living polymers react with difunctional monomers [12,13]. The norbornadiene dimer was employed as a difunctional monomer for the synthesis of star polynorbornene by ROMP [14].

AB_2-type copolymers, as one kind of star polymers, can be considered as two sidearms linked to the end of one polymer chain. One of those efficient methods to prepare miktoarm star polymer is to employ one or several “living”/controlled radical polymerization methods combined with functional group transformation technique

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using a heterofunctional initiator. Gnanou [15] reported an easy access to asymmetric stars and miktoarm stars by ATRP and chemical modification of the termini of ATRP-derived polymers. Pan [16–20] synthesized a series of ABC and A_2B_2 miktoarm star copolymers by combining ATRP or reversible addition–fragmentation chain-transfer (RAFT) polymerization with ROP, cationic ROP, or RAFT using maleic anhydride as linking agent. Wang [21] synthesized the amphiphilic ABC 3-miktoarm star terpolymer by the combination of ROP and "click" chemistry. Bai [22] reported the synthesis, characterization, and self-assembly of ion-bonded A_2B rod-coil copolymer. Tunca [23] presented a facile synthesis of AB_2 miktoarm star polymers through the combination of ATRP and ROP. Nomura [24] synthesized an AB_2 copolymer containing acetal-protected sugars prepared by the coupling of an end-functionalized ROMP copolymer with poly(ethylene glycol).

Recently, increasing attention has been devoted to find a general and easy approach to functionalize the end groups of polymers via ring-opening metathesis polymerization (ROMP). This method could prepare ROMP polymers with functionalized group on one (monotelechelic) or both ends (telechelic) of a polymer chain and with which the polymers could be attached to the other polymer structure easily, which could expand the scope of ROMP materials to more complex structure copolymers, such as star polymers, graft copolymers, multiblock copolymers, and others. However, there is still a challenge in the ability to control the structure with precision, because the facile backbiting and chain-transfer reactions occurred in ruthenium catalyzed ROMP of cycloolefin especially cyclooctene [25] arising from the structure and characteristics of monomers and chain-transfer agents (CTA) [26] or terminating agents (TA).

Generally, there have been three different strategies for the synthesis of end-functional polymers via ROMP in literatures. The first approach describes the use of CTAs to achieve telechelic polymers [27,28], whose disadvantage is that the polymer chain is not made in a living fashion, so a polydisperse product is obtained. The second approach is typically carried out first by exchanging the benzylidene on the metathesis catalyst for an alkylidene with the desired functionality, which could be then transferred directly onto one polymer chain end [29], but this strategy suffers from the necessity of synthesizing a corresponding catalyst for each new desired end-functional group. The third approach is the end-capping method, in which two routes are utilized to yield mono end-functional polymers. One is the direct and facile route involving the addition of a small molecule onto the end of the polymer chain by the reaction of TAs and the living chain end using ruthenium metathesis catalyst [26,30–32], where properly functionalized enol ethers or esters are the most used as the TAs. In addition, the acrylates were also used as TA for the preparation of semi-telechelic polymers made by ROMP [33]. The other is the newly developed synthetic route called as "sacrificial synthesis" based on the cleavage of second block from diblock copolymer ensuring the high degree of mono chain end-functionalization [34–40]. The former considered as more effective and relatively simple by comparison has been employed to prepare monotelechelic metathesis polymers bearing one functional end group, which further making for the formation of a few linear copolymers via a controlled polymerization technique as reported by several research groups. For instance, Grubbs [41] reported the preparation of linear poly(oxa)norbornenes-*block*-polystyrene or -poly(*tert*-butyl acrylate) copolymers via a combination of ROMP using an asymmetrical or a difunctional symmetrical TA and ATRP; Weck [42] synthesized linear poly(lactic acid)-*block*-poly(norbornene) copolymers by combining the ROMP of norbornene with ROP of lactide. To our knowledge, only one report [43] mentioned this end-capping method in the preparation of ABC 3-miktoarm star terpolymer, which was necessarily employed in combination of ROMP, ATRP, NMP and click chemistry to attain the target structure copolymers. Herein we present the practical protocol for preparation of a novel amphiphilic AB_2 star copolymer in combination of ROMP and ATRP technique as shown in Scheme 1. The poly(oxanorbornene)-based monotelechelic polymer was prepared via two different routes (methods A and B) as the hydrophobic arm with a dibromo-ended group, which was then employed as the macroinitiator for ATRP of 2-(dimethylamino)ethyl methacrylate (DMAEMA) to produce two hydrophilic arms. In addition, the micellar characteristics of the amphiphilic miktoarm star copolymers were investigated by using dynamic light scattering (DLS), atom force microscopy (AFM), and transmission electron microscopy (TEM) measurements.

2. Experimental

2.1. Materials

2,2-Bis(hydroxymethyl) propanoic acid (98%), 2-bromoisobutyryl bromide (97%), 2-(dimethylamino)ethyl methacrylate (DMAEMA, 97%), N,N-dimethyl 4-amidopyridine (DMAP, 98%), *cis*-1,4-butenediol (99%), 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDC · HCl, 99%), N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA, 98%), and benzylidene-bis(tricyclohexylphosphine) dichlororuthenium (first generation Grubbs catalyst, Ru^{1st}) were purchased from Aldrich or Alfa Aesar and used without purification. Copper(I) bromide (CuBr, Alfa Aesar, 97%) was purified by washing with glacial acetic acid, followed by absolute ethanol and ethyl ether, and then dried under vacuum. 2,2-Bis(2′-bromo-2′-methylpropionyloxy methyl) propionic acid [44] and 7-oxanorborn-5-ene-*exo*,*exo*-2,3-dicarboxylic acid dimethyl ester (ONBDM) [45,46] were synthesized according to the literature procedures. Solvents and reagents were distilled over drying agents under nitrogen prior to use: methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$), acetonitrile (CH_3CN), and *cis*-1,4-butenediol from calcium hydride, tetrahydrofuran (THF) from sodium/benzophenone. Triethylamine (Et_3N) was freshly distilled and dried by sieves.

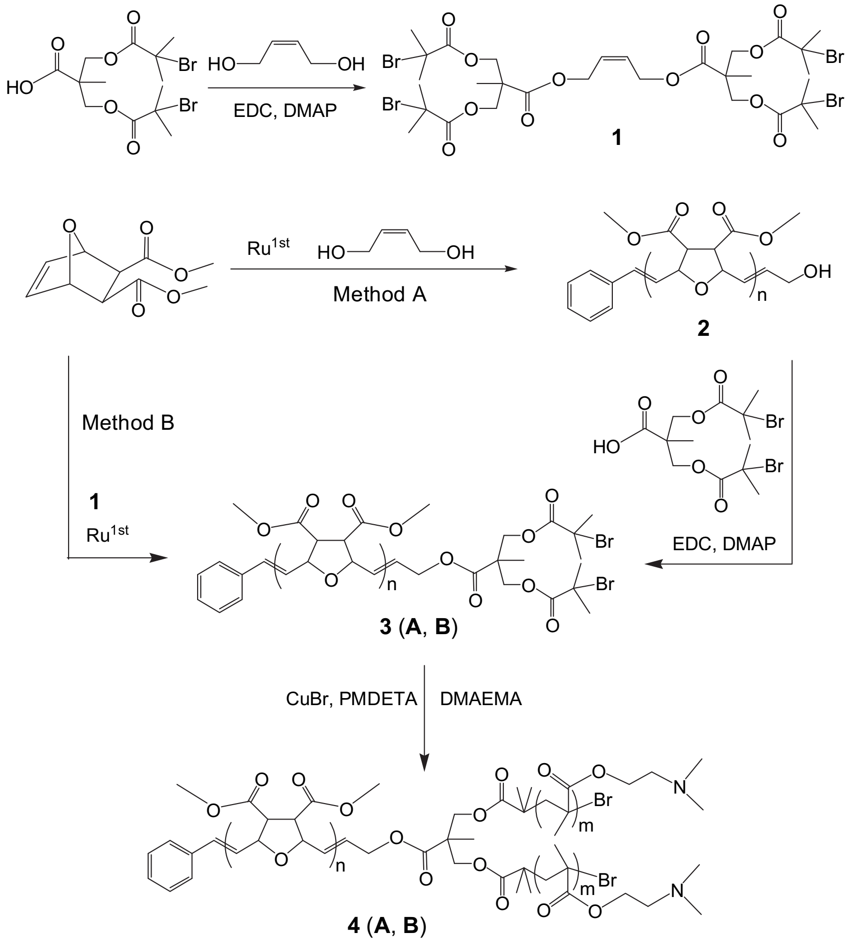
Polymerizations were carried out in Schlenk tubes under dry nitrogen atmosphere for ROMP and under vacuum for ATRP.

2.2. Characterization

^1H (300, 500 MHz) and ^{13}C (75 MHz) NMR spectra were recorded using tetramethylsilane as an internal standard in $CDCl_3$, CD_3COCD_3 or DMSO-d_6 on a Bruker DPX spectrometer. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (7.8 × 300 mm, 5 μm bead size; 10^3, 10^4, and 10^5 Å pore size). GPC measurements were carried out at 35 °C using THF as the eluent with a flow rate of 1.0 mL/min. The system was calibrated with polystyrene standards. The hydrodynamic diameters were determined by DLS analysis using a Malvern Zetasizer Nano-ZS light scattering apparatus (Malvern Instruments, U.K.) with a He–Ne laser (633 nm, 4 mW). AFM observations were performed on SPM AJ-III atomic force microscope at a measure rate of 1.0005 Hz in the tapping mode, and the AFM images were obtained at room temperature in air. TEM was performed on a JEM-2100 microscope operating at an acceleration voltage of 120 kV.

2.3. Synthesis of cis-2-butene-1,4-diol di[2,2-bis(2′-bromo-2′-methylpropionyloxy methyl)] propionic ester (**1**)

2,2-Bis(2′-bromo-2′-methylpropionyloxy methyl) propionic acid (5.18 g, 12 mmol) was dissolved in 60 mL of CH_3CN and *cis*-2-



Scheme 1. Synthesis of amphiphilic AB_2 star copolymers; EDC = 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride, DMAP = 4-dimethylaminopyridine, Ru^{1st} = first generation Grubbs catalyst, PMDETA = N,N,N′,N″,N″-pentamethyldiethylenetriamine, DMAEMA = 2-(dimethylamino)ethyl methacrylate.

butene-1,4-diol (0.352 g, 4.0 mmol) was added under nitrogen. DMAP (0.097 g, 0.8 mmol) and EDC · HCl (2.3 g, 12.0 mmol) were added to the solution at 0 °C and the resulting mixture was stirred at room temperature for 7 days. Solvent was removed under reduced pressure and the crude oil was dissolved in CH_2Cl_2. Then, the mixture was subsequently washed with 1 N HCl, saturated $NaHCO_3$ aq., and water twice. The organic layer was separated and dried over anhydrous $MgSO_4$ and concentrated. The residue was purified by column chromatography, eluting with 1:1 CH_2Cl_2/hexane on silica, to afford 2.0 g of product **1** as a viscous colorless liquid in 54% yield after solvent removal under reduced pressure. ^1H NMR (300 MHz, $CDCl_3$): δ (TMS, ppm) 5.76–5.72 (t, 2H, C*H*═C*H*), 4.76–4.74 (d, 4H, CH_2O), 4.40–4.29 (q, 8H, CH_2CO), 1.90 (s, 24H, C(CH_3)$_2$Br), 1.33 (s, 6H, CCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 172.02 (CH═CHCH$_2$O*C*O), 170.92 (O*C*OC(CH$_3$)$_2$Br), 128.01 (*C*H═*C*H), 66.25 (OCOC*C*H$_2$OCO), 60.73 (CH═CH*C*H$_2$), 55.30 (*C*(CH$_3$)$_2$Br), 46.68 (CH═CHCH$_2$OCO*C*), 30.63 (C(*C*H$_3$)$_2$Br), 17.81(OCOC*C*H$_3$).

2.4. General ring-opening metathesis polymerization procedures for syntheses of poly(oxanorbornene)-based monotelechelic polymers

In a nitrogen-filled Schlenk tube, a solution of first generation Grubbs catalyst (75.0 mg, 0.090 mmol) in 6 mL of CH_2Cl_2 was degassed with three freeze-vacuum-thaw cycles and then added to a degassed (with the same procedure as above) solution of monomer ONBDM (864.0 mg, 4.5 mmol) in 20 mL of CH_2Cl_2, to give a monomer concentration of 0.15 mol/L. After stirring at 30 °C for 20 min under nitrogen flow, TA *cis*-butene-1,4-diol (79.0 mg, 0.90 mmol) or **1** (824.0 mg, 0.90 mmol) was added as a solution in THF or CH_2Cl_2 in 4 mL. The reaction mixture was allowed to stir for 24 h. Then the reaction mixture was precipitated into a large volume of methanol, and the precipitate was isolated by filtration, dried under vacuum for 24 h to give the polymer as a solid.

2.4.1. Monohydroxyl-ended poly(7-oxanorborn-5-ene-exo,exo-2,3-dicarboxylic acid dimethyl ester) by method A (PONBDM$_n$-OH, **2**)

The product was recovered as a white powder in 95% yield. ^1H NMR (300 MHz, DMSO-d_6): δ (ppm) 7.41–7.23 (m, H_{Ar}), 5.80 (s, *trans*-C*H*═C*H* on polymer chain), 5.58 (s, *cis*-C*H*═C*H* on polymer chain), 4.86 (s, *cis*-C*H*OC*H* on each ONBDM unit), 4.54 (s, *trans*-C*H*OC*H* on each ONBDM unit), 3.92 (s, CH_2OH on one polymer chain end), 3.59 (s, OCH_3 on each ONBDM unit), 3.21 (s, C*H*COO on each ONBDM unit). GPC: $M_n = 10{,}100$, $M_w/M_n = 1.08$; NMR: $M_n = 10{,}600$.

2.4.2. Dibromo-ended poly(7-oxanorborn-5-ene-exo,exo-2,3-dicarboxylic acid dimethyl ester) by method B (PONBDM$_n$-2Br, **3B**)

The product was recovered as a tan powder in 92% yield. ^1H NMR (500 MHz, DMSO-d_6): δ (ppm) 7.46-–7.18 (m, H_{Ar}), 5.80 (s, *trans*-C*H*═C*H* on polymer chain), 5.58 (s, *cis*-C*H*═C*H* on polymer chain), 4.86 (s, *cis*-C*H*OC*H* on each ONBDM unit), 4.53 (s, *trans*-C*H*OC*H* on each ONBDM unit; CHCH_2OCO on one polymer end), 4.30–4.28 (d, CCH_2OCO on one polymer chain end), 3.58 (s, OCH_3

on each ONBDM unit), 3.21 (s, C*H*COO on each ONBDM unit), 1.86 (s, C(CH_3)$_2$Br on one polymer chain end), 1.30 (s, CCH_3 on one polymer chain end). GPC: $M_n = 9800$, $M_w/M_n = 1.09$; NMR: $M_n = 10{,}100$.

2.4.3. Preparation of dibromo-ended poly(7-oxanorborn-5-ene-exo,exo-2,3-dicarboxylic acid dimethyl ester) via esterification reaction by method A (PONBDM$_n$-2Br, **3A**)

The obtained polymer PONBDM$_n$-OH **2** (0.795 g, 0.075 mmol) was dissolved in 30 mL of CH_2Cl_2 and 2,2-bis(2′-bromo-2′-methylpropionyloxymethyl) propionic acid (1.17 g, 2.7 mmol) was added under nitrogen. DMAP (66.0 mg, 0.54 mmol) and EDC · HCl (518.0 mg, 2.7 mmol) were added to the solution at 0 °C and the resulting mixture was stirred at room temperature for 7 days. The product was precipitated twice from cold methanol, dried for 24 h in a vacuum oven at 35 °C to afford 700 mg of the monotelechelic dibromide end-functionalized polymer **3A** as a white powder in 96% yield. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) 7.44–7.26 (m, H_{Ar}), 5.80 (s, *trans*-C*H*═C*H* on polymer chain), 5.58 (s, *cis*-C*H*═C*H* on polymer chain), 4.85 (s, *cis*-C*H*OC*H* on each ONBDM unit), 4.53 (s, *trans*-C*H*OC*H* on each ONBDM unit; CHCH_2OCO on one polymer end), 4.29 (d, CCH_2OCO on one polymer chain end), 3.59 (s, OCH_3 on each ONBDM unit), 3.21 (s, C*H*COO on each ONBDM unit), 1.86 (s, C(CH_3)$_2$Br on one polymer chain end), 1.27 (s, CCH_3 on one polymer chain end). GPC: $M_n = 10{,}900$, $M_w/M_n = 1.09$; NMR: $M_n = 11{,}000$.

2.5. Preparation of amphiphilic star poly(7-oxanorborn-5-ene-exo, exo-2,3-dicarboxylic acid dimethyl ester)-block-bis[poly(2-(dimethylamino)ethyl methacrylate)] (PONBDM$_n$-b-(PDMAEMA$_m$)$_2$, **4**) via atom transfer radical polymerization using **3** as macroinitiator

Macroinitiator **3A** or **3B** in 1.0 mL of THF, monomer DMAEMA, PMDETA and CuBr in 0.5 mL of CH_3OH were charged into a Schlenk tube. After degassing of the mixture by three freeze-pump-thaw cycles, the tube was sealed under vacuum and then heated at 50 °C for 12–36 h. The reaction was quenched by removal of heat and exposure to air. The mixture was diluted in 15 mL of $CHCl_3$ followed by passing through a short silica column to remove the copper residues. The purified copolymer was precipitated in petroleum ether twice, and then dried under vacuum for 24 h to give the AB$_2$ star copolymer **4** PONBDM$_n$-*b*-(PDMAEMA$_m$)$_2$ as a white solid with the monomer conversion ranging from 18% to 70%. ^{1}H NMR (500 MHz, CD_3COCD_3): δ (ppm) 7.58–7.18 (m, H_{Ar}), 5.94 (s, *trans*-C*H*═C*H* on polymer chain), 5.66 (s, *cis*-C*H*═C*H* on polymer chain), 5.05 (s, *cis*-C*H*OC*H* on each ONBDM unit), 4.66 (s, *trans*-C*H*OC*H* on each ONBDM unit; CH═CHCH_2OCO), 4.07 (s, COOCH_2 on each DMAEMA unit; CCH_2OCO), 3.66 (s, OCH_3 on each ONBDM unit), 3.21 (s, C*H*COO on each ONBDM unit), 2.58 (s, CH_2N on each DMAEMA unit), 2.28 (s, N(CH_3)$_2$ on each DMAEMA unit), 1.97–1.88 (d, CH_2C on each DMAEMA unit), 1.10–0.96 (d, CH_3CBr on each DMAEMA unit; CCH_3, OCOC(CH_3)$_2$).

2.6. Self-assembly of amphiphilic AB$_2$ star copolymer

In a typical experiment, the copolymers were dissolved in THF at room temperature to make a polymer solution at 0.2 wt%. Selective solvent of water was then added to the copolymer solution under vigorous stirring at a rate of 1 drop every 10 s to give a content of 40 mg/L, followed by further vigorous stirring for 30 min and standing overnight prior to the measurements of DLS, AFM and TEM. Finally the solution was filtered through 0.45 μm Millipore filter.

3. Results and discussion

3.1. Synthesis of symmetrical tetrabromo-functionalized unsaturated diester (*1*)

The *cis*-butenediol-based diester with four α-bromoisobutyryl groups was prepared as the synthetic route illustrated in Scheme 1. Simple esterification of the commercially available *cis*-2-butene-1,4-diol with 1.5 equivalent of the prepared 2,2-bis(2′-bromo-2′-methylpropionyloxymethyl) propionic acid resulted in the formation of compound **1** in 54% yield. EDC · HCl was employed as a condensation agent, because the reaction was carried out under mild conditions and the urea derivative can be easily removed from the reaction mixture by washing with water [47]. The symmetrical tetrabromo-functionalized unsaturated diester **1** was chosen as TA for ROMP resulting in the formation of the novel monotelechelic polymer with dibromo-functionalities, which would be the effective agent for initiating ATRP of styrene, methyl methacrylate, and a variety of other monomers followed as the previous reports [41,48]. The structure of **1** was confirmed by ^{1}H, ^{13}C NMR spectroscopy. The characteristic resonances for the protons of alkene, methylene, and methyl were observed at their corresponding positions in Fig. 1A.

3.2. Preparation of hydroxyl- or dibromo-terminated monotelechelic polymers via ROMP

One of the advantages in using ROMP with functionalized symmetrical TA for the preparation of monotelechelic polymers is the ability to directly incorporate the desired functional group onto the polymer by reaction with the living chain end without need to perform the complicated postpolymerization transformations [41]. Tunca [43] utilized this end-capping method in the preparation of 3-miktoarm star terpolymer by using the combination of ROMP, ATRP, NMP, and click chemistry. Herein, we also demonstrate the effectiveness of this strategy for the synthesis of monotelechelic ROMP polymer with dibromo-terminated functionality, PONBDM$_n$-2Br, which can be used as macroinitiator to initiate ATRP of DMAEMA, fabricating the expected star copolymer PONBDM$_n$-*b*-(PDMAEMA$_m$)$_2$, where *n* and *m* indicate the repeating unit numbers of the respective blocks.

ROMP of ONBDM was carried out under an inert atmosphere at 30 °C for 20 min in 30 mL of CH_2Cl_2 to give an initial monomer concentration of 0.15 mol/L, followed by addition of 10 equiv of TA *cis*-butene-1,4-diol (in method A) or **1** (in method B). The reaction mixture was stirred for an additional 24 h, and then the product, **2** or **3B**, was precipitated and recovered by filtration with good yield of 95% and 92%, respectively, after dried under vacuum. The structure of the polymers obtained from both routes (methods A and B) could be confirmed by ^{1}H NMR analysis as shown in Fig. 1B and C. The alkene proton signals of the oxanorbornene ring appeared approximately at 6.45 ppm. Upon ring-opening and subsequent polymerization, these proton signals shifted upfield to approximately 5.80–5.58 ppm (H_f) in both Fig. 1B and C, indicating the polymerization had occurred.

For product **3B** obtained from method B, the resonance of methylene protons attached to the ester bond (CCH_2OCO) shifted from 4.40 ppm in TA **1** to 4.30 ppm (H_c) in the polymer chain end, and the resonance of methyl protons adjacent to bromide (C(CH_3)$_2$Br) also appeared at 1.86 ppm (H_e) in Fig. 1B, which meant the α-bromoisobutyrate segment from TA **1** has been successful incorporated into the polymer chain end and the dibromo-containing monotelechelic polymer **3B** was directly prepared by method B. The capping efficiency (CE) [31] for method B was determined by comparing the integration of the signal from the

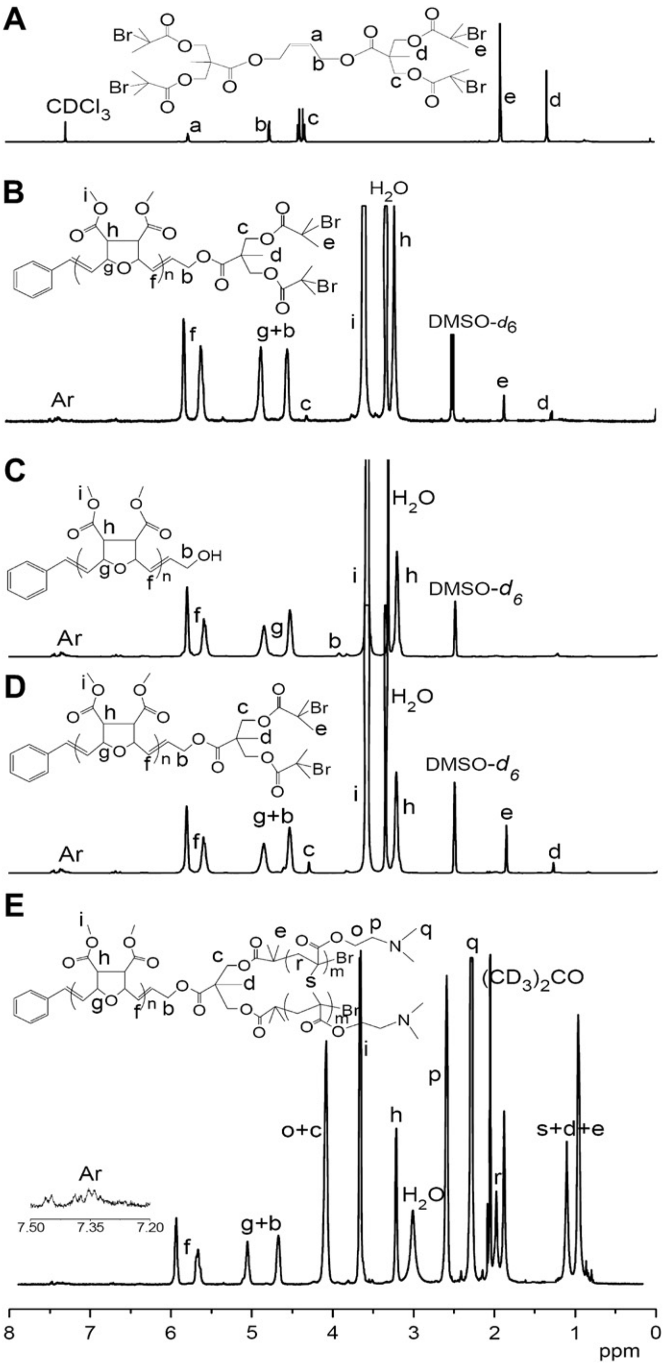


Fig. 1. ^1H NMR spectra for (A) *cis*-2-butene-1,4-diol di[2,2-bis(2′-bromo-2′-methylpropionyloxy methyl)] propionic ester (**1**), (B) dibromo-ended poly(7-oxanorborn-5-ene-*exo*,*exo*-2,3-dicarboxylic acid dimethyl ester) by method B (PONBDM$_n$-2Br, **3B**), (C) monohydroxyl-ended PONBDM by method A (PONBDM$_n$-OH, **2**), (D) dibromo-ended PONBDM by method A (PONBDM$_n$-2Br, **3A**), (E) PONBDM-*block*-bis[poly(2-(dimethylamino) ethyl methacrylate)] using **3A** as macroinitiator (PONBDM$_n$-*b*-(PDMAEMA$_m$)$_2$, **4A**).

Table 1
Synthesis and characterization of monotelechelic poly(7-oxanorborn-5-ene-*exo*,*exo*-2,3-dicarboxylic acid dimethyl ester) (PONBDM$_n$) using Grubbs ruthenium catalyst and two different terminating agents (TA).[a]

Sample	TA	Yield (%)	$M_{n,th}$[b]	$M_{n,GPC}$[c]	M_w/M_n[c]	$M_{n,NMR}$[d]	CE (%)[e]
2	*cis*-butene-1,4-diol	95	9200	10100	1.08	10600	94
3A[f]	–	–	–	10900	1.09	11000	94
3B	**1**	92	9300	9800	1.09	10100	67

[a] Reaction conditions: Feed ratio of monomer ONBDM (M) to first generation Grubbs catalyst (C) $[M]_0:[C]_0 = 50:1$, $[M]_0 = 0.15$ mol/L, $[TA]_0 = 0.03$ mol/L, solvent = 30 mL, polymerization temperature = 30 °C, polymerization time = 24 h.

[b] $M_{n,th} = ([M]_0:[C]_0) \times M_{monomer} \times \text{yield}\ \% + M_{TA}/2$, where $M_{monomer} = 192$, $M_{TA(\mathbf{1})} = 916$, and $M_{TA(cis\text{-butene-1,4-diol})} = 88$ are the molar masses of monomer ONBDM, TA **1**, and TA *cis*-butene-1,4-diol, respectively.

[c] Determined by gel permeation chromatography (GPC) in THF relative to monodispersed polystyrene standards.

[d] $M_{n,NMR} = (S_f/2)/(S_{Ar}/5) \times M_{monomer} + M_{TA}/2$ was obtained by ^1H NMR spectroscopy.

[e] Capping efficiency (CE) was determined by ^1H NMR spectroscopy.

[f] Product obtained from the esterification of ring-opening metathesis polymer **2**.

phenyl protons at 7.46–7.18 ppm (S_{Ar}, 5H) on one polymer chain end to a signal of the diagnostic methyl protons at 1.86 ppm (S_e, 12H) from TA **1**, thus it was calculated from the ^1H NMR spectrum (Fig. 1B) as $CE_{\mathbf{3B}} = [(S_e/12)/(S_{Ar}/5)] \times 100\% = 67\%$ (Table 1). This value of CE is relatively low, and it has not an obvious accretion by changing the reaction conditions, whatever tried in lower or higher reaction temperature, shorter or longer reaction time. We deemed that the large terminal recognition unit of TA **1** would sterically reduce the reactive probability between the living polymer chain end and the bulky recognition unit. Although this one step route (method B) is simple, the termination efficiency is dissatisfactory. Accordingly, the other route (method A) including two steps was selected to achieve the same monotelechelic polymer **3**.

For the first step in method A, ROMP was performed under the same conditions as those in method B except for using *cis*-butene-1,4-diol as TA. The characteristic ^1H NMR data of the obtained hydroxyl-terminated monotelechelic polymer PONBDM$_n$-OH **2** were demonstrated as previously stated, and most resonances of the protons from monomer ONBDM units were similar with those of polymer **3B**. Only the resonance of methylene protons adjacent to hydroxyl group ($CH{=}CHCH_2OH$) was observed at 3.92 ppm (H_b, 2H) in Fig. 1C, revealing the successful incorporation of TA segment into the polymer chain end. CE for this route could be formulated as $CE_{\mathbf{2}} = [(S_b/2)/(S_{Ar}/5)] \times 100\% = 94\%$, and this excellent CE may be ascribed to the sterically unencumbered TA. As the second step in method A, the esterification reaction between the end group hydroxyl on polymer **2** with 2,2-bis(2′-bromo-2′-methylpropionyloxy methyl) propionic acid was conducted under conventional conditions by using EDC · HCl as the condensation agent to yield the monotelechelic polymer **3A**. After esterification, ^1H NMR spectrum (Fig. 1D) shown that three new resonances corresponding to the protons CCH_2OCO, $C(CH_3)_2Br$, and CCH_3 appeared at 4.29 ppm (H_c), 1.86 ppm (H_e), and 1.27 ppm (H_d) in Fig. 1D, respectively; while the signal of methylene protons adjacent to the hydroxyl group ($CH{=}CHCH_2OH$) at 3.92 ppm (H_b) in Fig. 1C disappeared, and the signal of the same methylene protons for $CH{=}CHCH_2OCO$ (H_b) was combined downfield with that at 4.53 ppm. The value of CE for **3A** could be calculated from the ^1H NMR spectrum (Fig. 1D) by using the same formula as that for **3B**, i.e. $CE_{\mathbf{3A}} = [(S_e/12)/(S_{Ar}/5)] \times 100\% = 94\%$, which is consonant with $CE_{\mathbf{2}}$. These observation indicated that the end group of hydroxyl has been converted into ester bond completely, and the relevant product polymer **3A** was formed almost quantitatively with much higher CE than that of **3B**, strongly supported that method A is more effective than method B.

The molecular weights ($M_{n,NMR}$) of the polymers were estimated from ^1H NMR spectra. By comparing the integral intensity of the alkene protons (H_f, 2 protons for each ONBDM unit) ($S_f/2$) from the monomer unit at 5.80–5.58 ppm to the integral intensity of the phenyl protons (H_{Ar}, 5 protons) ($S_{Ar}/5$) from the end-group at 7.46–7.18 ppm, the ratio of $(S_f/2)/(S_{Ar}/5) = n$, which is the average degree of polymerization (DP_n) of monomer ONBDM, was used to determine the number-average molecular weight of the polymers,

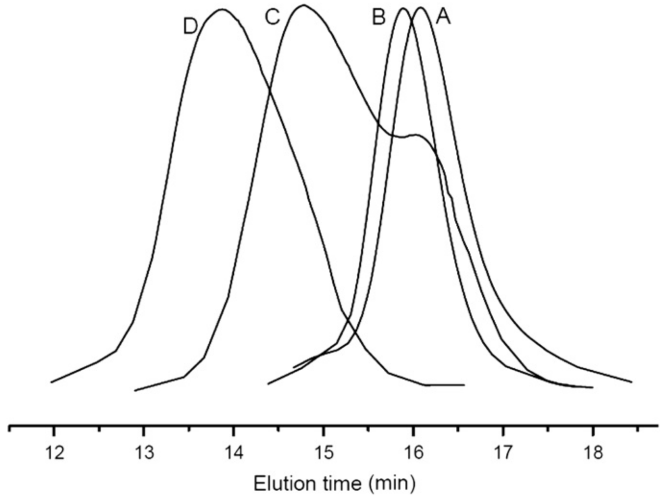


Fig. 2. Gel permeation chromatography (GPC) traces of (A) polymer **3B** ($M_n = 9800$, $M_w/M_n = 1.09$); (B) polymer **3A** ($M_n = 10{,}900$, $M_w/M_n = 1.09$); (C) Copolymer **4B** using **3B** as the macroinitiator ($M_n = 25{,}100$, $M_w/M_n = 1.22$); (D) AB_2 copolymer **4A** using **3A** as the macroinitiator ($M_n = 31{,}000$, $M_w/M_n = 1.12$).

Table 2
Atom transfer radical polymerization of 2-(dimethylamino) ethyl methacrylate (DMAEMA) using dibromo-ended polymer **3** as macroinitiator in THF/CH_3OH.[a]

Sample	t (h)	Conversion (%)	$M_{n,GPC}$[b]	M_w/M_n[b]	$M_{n,NMR}$[c]
$PONBDM_{55}$-*b*-$(PDMAEMA_{75})_2$[d]	12	31	25,500	1.10	32,000
$PONBDM_{55}$-*b*-$(PDMAEMA_{110})_2$[d]	24	46	31,000	1.12	45,500
$PONBDM_{55}$-*b*-$(PDMAEMA_{150})_2$[d]	36	70	43,500	1.23	58,300
$PONBDM_{51}$-*b*-$(PDMAEMA_{74})_2$[e]	12	18	25,100	1.22	27,000

[a] Reaction conditions: [**3**]:[DMAEMA]:[CuBr]:[PMDETA] = 1:400:2:2, polymerization temperature = 50 °C.

[b] Measured by GPC analysis in THF.

[c] $M_{n,NMR} = 2\,m \times M_{DMAEMA} + M_{n(\mathbf{3})} = (S_P/S_f) \times n \times M_{DMAEMA} + M_{n(\mathbf{3})}$ was obtained by ^1H NMR analysis, where $n = (S_f/2)/(S_{Ar}/5)$ represents the average number of ONBDM repeating units, $M_{DMAEMA} = 157$ is the molar mass of DMAEMA, $M_{n(\mathbf{3A})} = 11{,}000$ and $M_{n(\mathbf{3B})} = 10{,}100$ are the molecular weight of macroinitiator **3A** and **3B**, respectively.

[d] Using **3A** as the macroinitiator.

[e] Using **3B** as the macroinitiator.

$M_{n,NMR} = (S_f/2)/(S_{Ar}/5) \times M_{monomer} + M_{TA}/2$, and the values were shown in Table 1, which were comparatively in accordance with the theoretical ones ($M_{n,th}$) and those measured by GPC ($M_{n,GPC}$). The polydispersity indices of polymers were low to 1.09, and the monomodal GPC curves for polymer **3B** and **3A** are shown in Fig. 2A and B, respectively.

3.3. Preparation of amphiphilic AB_2 star copolymers via ATRP

In recent years, block copolymers have attracted much attention due to their applications as stabilizers in emulsions or dispersions and drug delivery carriers, etc [49,50]. The amphiphilic block copolymers containing hydrophilic PDMAEMA block are of particular scientific interest, since they are sensitive to temperature and pH [51]. ATRP is commonly used to produce amphiphilic block or graft copolymers with PDMAEMA as a hydrophilic block in our previous reports [52,53].

For synthesis of AB_2 star copolymers with PDMAEMA blocks, the ATRP of DMAEMA was carried out by using dibromo-ended polymer $PONBDM_n$-2Br, **3A** ($M_n = 10900$, $M_w/M_n = 1.09$) as macroinitiator and CuBr/PMDETA as catalyst/ligand at 50 °C for 12–36 h in THF/CH_3OH. The mixture of THF/CH_3OH was chosen as solvent because its good ability to dissolve the monomer, catalyst, macroinitiator, and the produced polymer. The homogeneous reaction mixture was thus retained throughout the whole process of reaction even the viscosity of the mixture increased with progress of polymerization. The resulting mixture was diluted with $CHCl_3$ followed by passing through a short silica column to remove the copper residues, and then precipitated from petroleum ether to remove the excess of monomer affording the AB_2 star copolymer **4A** $PONBDM_n$-*b*-$(PDMAEMA_m)_2$ as a white solid. The yield of product was increased from 18 to 70% with the extension of polymerization time from 12 h to 36 h (Table 2).

To confirm the formation of the copolymers, their ^1H NMR spectra were measured and the representative spectrum for $PONBDM_n$-*b*-$(PDMAEMA_m)_2$ was shown in Fig. 1E. The structure of the copolymer was verified through the resonances of characteristic protons CH_2N and $N(CH_3)_2$ from the block of PDMAEMA at 2.58 (H_p) and 2.28 ppm (H_q), respectively. The integration area ratio of these resonances of 2.0:6.1 was in accordance with the ratio of corresponding protons of 2:6. Importantly, the signal of methylene protons CCH_2OCO at 4.29 ppm (H_c) in Fig. 1D was disappeared after ATRP and combined upfield with that at 4.07 ppm (H_{c+o}) in Fig. 1E. By comparing the integral intensity of the methylene protons from one PDMAEMA chain at 2.58 ppm (H_p, 2 protons for each DMAEMA unit) [$S_P/2$] to that of the alkene protons from PONBDM at 5.94–5.66 ppm (H_f, 2 proton for each ONBDM unit) [$S_f/2$], the average degree of polymerization (DP_n) of the monomer DMAEMA can be written as follows: $DP_n = m = [(S_P/2)/2]/(S_f/2) \times n = (S_P/2)/S_f \times n$, which was further used to determine the number-average molecular weight of the polymers, $M_{n,NMR} = 2\,m \times M_{DMAEMA} + M_{n(\mathbf{3})} = (S_P/S_f) \times n \times M_{DMAEMA} + M_{n(\mathbf{3})}$.

The representative GPC curve in Fig. 2D showed the molecular weight and molecular weight distribution of the AB_2 star copolymer prepared from the macroinitiator **3A**. After polymerization, the molecular weights of the copolymers prepared from **3A** are shifted to high molecular weight positions along with the extension of polymerization time (Table 2), and no peak attributed to the starting macroinitiator **3A** was observed in the monomodal distribution curve as shown in Fig. 2D, which meant the macroinitiator has been completely converted to the corresponding AB_2 star copolymers. The values of M_n measured by GPC were lower than those estimated by NMR ($M_{n,NMR}$) as shown in Table 2, that is likely due to somewhat the adsorption of PDMAEMA blocks onto the GPC column as depicted in the lag curve 2D, which would result in an increase in retention time and lead to lower detected molecular weights [54,55]. Furthermore, the AB_2 star copolymers in three cases (Table 2) have reasonable low molecular weight distributions within 1.10–1.23.

The initiation efficiency for macroinitiator **3A** in the ATRP process could be ascertained from the ^1H NMR spectrum (Fig. 1E) of polymer **4A**. The resonance corresponding to the protons CCH_2OCO at 4.29 ppm (H_c) in Fig. 1D disappeared completely because it was combined upfield with that at 4.07 ppm in Fig. 1E, indicating the initiation was occurred quantitatively. In addition, no subtile peak attributed to the starting macroinitiator residue was observed in the monomodal GPC chromatogram Fig. 2D, which meant the macroinitiator was completely consumed and could be considered as a positive evidence for the formation of the expected AB_2 star copolymers.

For comparison, the macroinitiator **3B** with lower capping efficiency than **3A** was also used to initiate the ATRP of DMAEMA using a CuBr/PMDETA catalyst system, yielding copolymer **4B**. As expected, a bimodal distribution in GPC chromatogram was depicted in Fig. 2C, where a shoulder should be originated from the PONBDM residue without end-capped dibromo-functionalized group, and the primary peak is from the copolymer with the molecular weight of 25,100.

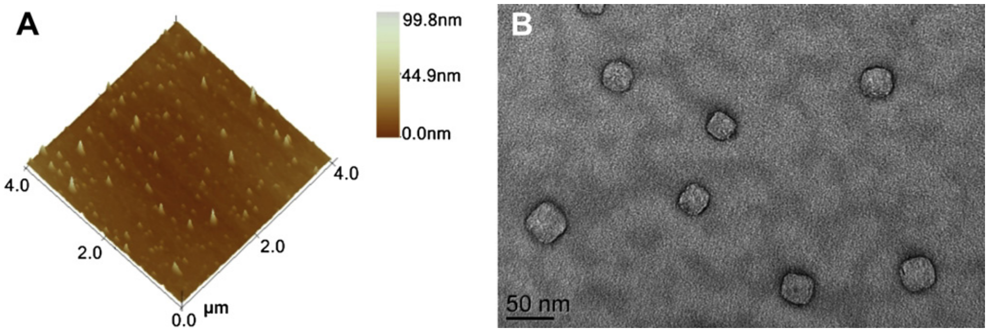


Fig. 3. Aggregates formed by the self-assembly of AB_2 star copolymer $PONBDM_{55}$-$(PDMAEMA_{110})_2$ with concentration of 40 mg/L in THF/water: (A) AFM image, (B) TEM image.

3.4. Aggregation behavior

Amphiphilic block copolymers are able to self-assemble into a variety of stable nanostructures when dissolved in a selective solvent due to the association of the insoluble core-forming blocks. Aggregate morphologies of amphiphilic block copolymers, including spherical micelles, cylinders, vesicles, and other complex structures [56,57], are closely correlated to the copolymer composition and the chain length ratio of the hydrophilic blocks to hydrophobic blocks [58]. When the volume ratio of the hydrophobic block to the hydrophilic block is high, vesicles and other complex structures are frequently observed, whereas micelles are commonly obtained [56,57]. In the present study, two AB_2 star copolymers of $PONBDM_{55}$-*b*-$(PDMAEMA_{110})_2$ and $PONBDM_{55}$-*b*-$(PDMAEMA_{75})_2$ with a fixed chain length of hydrophobic PONBDM and various hydrophilic PDMAEMA chain lengths, with the low volume ratios of the hydrophobic block to the hydrophilic block, were selected to investigate the effect of copolymer composition on their self-assembly behaviors. Both the PDMAEMA block and the PONBDM block are totally soluble in THF, and the PDMAEMA block is also soluble in water, while the block PONBDM is insoluble in water. The solubility discrepancy between the PDMAEMA and PONBDM blocks in $PONBDM_n$-*b*-$(PDMAEMA_m)_2$ copolymer provides a possibility of self-aggregation to form micelles in the selective solvent of water. Thus the aggregates were prepared by adding water into the copolymer solution of THF.

DLS measurements provided a dependence of the average hydrodynamic radius on PDMAEMA block length. The hydrodynamic diameters of two polymer aqueous solution samples $PONBDM_{55}$-*b*-$(PDMAEMA_{110})_2$ and $PONBDM_{55}$-*b*-$(PDMAEMA_{75})_2$ aggregates were estimated by DLS measurements affording an average micelle diameter of 330 nm and 130 nm, respectively. It was known that PONBDM blocks would be tightly coiled in the aggregate core, with the PDMAEMA blocks loosely packed around it, and the overall diameter represented the core dimension and the shell thickness. The shell thickness of the micelle increased with the increase in DMAEMA block length, which resulted in the larger average hydrodynamic diameter of the polymeric micelles.

The morphology of AB_2 star copolymers $PONBDM_n$-*b*-$(PDMAEMA_m)_2$ in THF/water was examined by AFM and TEM. Fig. 3A showed AFM image of aggregates formed by copolymer $PONBDM_{55}$-*b*-$(PDMAEMA_{110})_2$ bearing two longer PDMAEMA blocks, which was prepared from the macroinitiator **3A**, with concentration of 40 mg/L. A spherical morphology with a diameter of around 90 nm and the average height of 50 nm was observed, and the aggregates were separated and randomly deposited on the mica surface as spherical micelles, comparatively uniform in size. TEM image clearly showed that the morphology was a spherical structure with the average diameter of 50 nm, which is close to the average height deduced from AFM, and a higher transmission in the center of aggregates than their periphery was observed in Fig. 3B. This morphology is consistent with what was expected for the micelles or particles.

The sample preparation could contribute to the different micelle sizes detected by TEM and DLS. DLS measurements were carried out in solution, where the PONBDM core was highly swollen by solvent and was thus very flexible, while deposition of the polymer self-assemblies onto the carbon grid implied that sample drying could cause shrinkage of the micelles and thus smaller diameter detected by TEM.

4. Conclusion

This work reported the synthesis of a novel AB_2 star copolymer with two sidearms linked to the end of one polymer chain via combination of ROMP and ATRP. Two different routes (methods A and B) were employed to prepare the poly(oxanorbornene)-based monotelechelic polymers. Firstly, ROMP of ONBDM in the presence of di[2,2-bis(2′-bromo-2′-methylpropionyloxymethyl)] propionic ester (**1**) acted as TA was performed to directly produce the dibromo-ended polymer $PONBDM_n$-2Br by method B in one step, but only 67% of the capping efficiency (CE) for polymer was achieved in this procedure, which meant there existed 33% of homopolymer PONBDM without end-capping group. Then, a two-step route referred as method A was considered as alternative. In the first step, *cis*-butene-1,4-diol was utilized as TA to provide the monotelechelic polymer $PONBDM_n$-OH with one hydroxyl end-functionality, and the value of CE was reached up to 94%; in the second step, the hydroxyl end-functionality of polymer was transformed quantitatively into dibromide end-functionalities via esterification reaction. Although it is more convenient to create the monotelechelic polymer with dibromo-ended group terminated by TA **1** than TA *cis*-butene-1,4-diol, the results of NMR analysis showed the CE of the produced polymer by *cis*-butene-1,4-diol was much higher than that by **1**. The dibromo-ended ROMP polymers were employed as the macroinitiator to initiate the ATRP of DMAEMA, producing star copolymers $PONBDM_n$-*b*-$(PDMAEMA_m)_2$. These AB_2 star copolymers can self-assemble in THF/water, and the morphologies of aggregates were revealed by AFM and TEM measurements.

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