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ARTICLE

Synthesis of doubly thermo-responsive schizophrenic diblock copolymer based on poly[*N*-(4-vinylbenzyl)-*N*,*N*-diethylamine] and its temperature-sensitive flip-flop micellization

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Abstract: Synthesis of doubly thermo-responsive schizophrenic diblock copolymer of poly(*tert*-butyl methylacrylate)-*block*-poly[*N*-(4-vinylbenzyl)-*N*,*N*-diethylamine] (P*t*BMA-*b*-PVEA) by reversible addition-fragmentation chain transfer (RAFT) polymerization and its temperature-sensitive flip-flop micellization are discussed. By employing 4-cyano-4-[(dodecylsulfanylthiocarbonyl) sulfanyl] pentanoic acid as RAFT agent, the schizophrenic P*t*BMA-*b*-PVEA diblock copolymers with different block length were prepared. The poly(*tert*-butyl methylacrylate) (P*t*BMA) block exhibits insoluble-to-soluble phase transition at the upper critical solution temperature (UCST) and the poly[*N*-(4-vinylbenzyl)-*N*,*N*-diethylamine] (PVEA) block exhibits soluble-to-insoluble phase transition at the lower critical solution temperature (LCST) in methanol, respectively. At temperature below the UCST of the P*t*BMA block, P*t*BMA@PVEA micelles containing a P*t*BMA core and a PVEA corona are formed in methanol. At temperature above the UCST of the P*t*BMA block and while below the LCST of the PVEA block, P*t*BMA-*b*-PVEA is molecularly soluble in methanol. At temperature above the LCST of the PVEA block, the inverse PVEA@P*t*BMA micelles containing a PVEA core and a P*t*BMA corona are formed. The polymerization degree of the P*t*BMA block or the PVEA block affecting the UCST/LCST of the schizophrenic diblock copolymer and the size of the P*t*BMA@PVEA or PVEA@P*t*BMA micelles is investigated.

Introduction

Thermo-responsive polymers, which can change their solubility or morphology in solvent when temperature steps across a critic temperature, have aroused great interest due to their important applications such as catalysis, drug delivery, sensors, intelligent gels, and smart materials.[1] Generally, two kinds of thermo-responsive polymers, one of which shows soluble-to-insoluble phase transition in solvent at the lower critical solution temperature (LCST), and the another undergoes reverse insoluble-to-soluble phase transition in solvent at the upper critical solution temperature (UCST), are classified.[2,3] Those bearing the amide group form the largest group of LCST-type thermo-responsive polymers,[2] in which poly(*N*-isopropylacrylamide) (PNIPAM) exhibiting LCST at 32 °C in water is the most popular.[4-6] Besides, poly(vinyl ether)s,[7] poly(ethylene glycol) analogues,[8] poly(2-oxazoline)s,[9] and poly(*N*-vinylcaprolactam)[10] in water, and poly(*n*-butylmethacrylate) (P*n*BMA)[11] and poly(ethylene oxide) (PEO)[12] in ionic liquid have been demonstrated to display LCST-type phase transition. At most cases, the LCST-type phase transition is triggered by the dissociation of hydrogen bond between the polymer chains and the solvent molecules when temperature increases above LCST. In contrast to the large number of reports on LCST-type polymers, UCST-type polymers are sparsely discussed,[3] and only a few examples of UCST-type polymers such as zwitterionic polysulfobetaines[13-15], ureido functionalized polymers[16] and poly(*N*-acryloylglycinamide)[17] in water, poly(vinylcyclopropane)s[18] and poly(methyl methacrylate)[19,20] in the alcohol/water mixture, poly(ethylene glycol) analogues[21] in alcohols and PNIPAM[22] in ionic liquid have been reported. Generally, the UCST-type phase transition is based on intra- and inter- chain interactions through hydrogen bonding or electrostatic attractions. Besides the LCST-type and UCST-type thermo-responsive polymers, thermo-responsive block copolymers containing more than one thermo-responsive blocks have been synthesized by the controlled radical polymerization (CRP) techniques such as atom transfer radical polymerization (ATRP),[23-25] nitroxide-mediated polymerization (NMP)[26] and reversible addition-fragmentation chain transfer (RAFT) polymerization[27-31]. Compared with the thermo-responsive block copolymers containing one thermo-responsive block,[32-35] those containing two different thermo-responsive blocks called

doubly thermo-responsive block copolymers are obviously more interesting, since the multiplex temperature-triggered self-assembly is reasonably expected.

The so-called 'schizophrenic' block copolymers are interesting,[36] because they can undergo flip-flop micellization upon the slight change in temperature, solution pH and/or ionic strength. Since schizophrenic block copolymer was first reported by Armes and coworkers in 1998,[37] a lot of schizophrenic block copolymers containing two pH-responsive blocks,[38-43] two thermo-responsive blocks,[44-53] two salt-responsive blocks,[54] one pH- plus one thermo-responsive blocks,[55-62] one photo- plus one thermo-responsive block,[63] and one pH- plus one salt-responsive blocks[37,64] have been prepared. For examples, the self-assembly of the schizophrenic block copolymers of poly(N-isopropylacrylamide)-*block*-poly{3-[N-(3-methacrylamidopropyl)-N,N-dimethyl]ammoniopropane sulfonate},[44,45] poly[sulfobetaine methacrylate]-*block*-[2-(N-morpholino)ethyl methacrylate],[46] poly(N-isopropylacrylamide)-*block*-poly(sulfobetaine methacrylate),[47] poly(N,N-diethylacrylamide)-*block*-poly[3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate],[48] poly(methoxy oligoethylenegylol methacrylate)-*block*-poly(dimethylaminoethyl methacrtylate)[49] and poly(oligo(ethylene glycol) methacrylate-*co*-2-(2-methoxyethoxy)ethyl methacrylate)-*block*-poly(N-(3-(dimethylamino)propyl) methacrylamide)[50] in water, and poly(ethylene oxide)-*block*-poly(N-isopropylacrylamide)[51] and poly(benzyl methacrylate)-*block*-poly(N-isopropylacrylamide-*random*-acryl amide)[52] in ionic liquid, have been checked and their flip-flop micellization has been demonstrated. These temperature-switchable schizophrenic block copolymers consisting of a UCST-type block and a LCST-type block are particularly attractive, since the flip-flop micellization can be achieved by simply changing the solution temperature.[49] However, these temperature-switchable schizophrenic block copolymers showing flip-flop micellization are relatively limited,[44-52] and the reason is possibly due to the UCST-type and LCST-type blocks in the block copolymer being not well matched and controlled synthesis of such a qualified doubly thermo-responsive schizophrenic block copolymer being not an easy thing.

In our previous study,[65-67] a new thermo-responsive polymer of poly[N-(4-vinylbenzyl)-N,N-diethylamine] (PVEA) was prepared, and it was found that PVEA exhibited LCST-type phase transition in methanol and its LCST was dependent on polymer molecular weight and polymer concentration. In this contribution, the doubly thermo-responsive schizophrenic diblock copolymer of poly(tert-butyl methylacrylate)-*block*-poly[N-(4-vinylbenzyl)-N,N-diethylamine] (PtBMA-*b*-PVEA), in which the poly(tert-butyl methylacrylate) (PtBMA) block shows UCST and the PVEA block exhibits LCST in methanol, was prepared by sequential

RAFT polymerization, and its temperature-sensitive flip-flop micellization in methanol was demonstrated. To the best of our knowledge, PtBMA-*b*-PVEA may be the first example showing doubly thermo-responsive schizophrenic behavior in the organic solvent of methanol. Comparing with the thermo-responsive diblock copolymer showing schizophrenic micellization in water,[49] PtBMA-*b*-PVEA has some potentials such as to be used as switchable stabilizer for solvophobic polymeric colloids dispersed in alcoholic solvent.

Experimental

Materials. The monomer of *tert*-butyl methacrylate (tBMA, >98%, Alfa Aesar) was purified by distilling under vacuum prior to use. The VEA monomer (Scheme S1) was synthesized by the nucleophilic substitution reaction of chloromethylstyrene (CMS >97%, Alfa) and diethylamine (DEA, >99.5%, Tianjin Chemical Corp) as discussed elsewhere,[66] and the ^{1}H NMR spectrum of VEA can be found in Fig. S1. The RAFT agent of 4-cyano-4-[(dodecylsulfanylthiocarbonyl) sulfanyl] pentanoic acid (CDTPA, Scheme S2) was synthesized as discussed elsewhere.[68] The initiator of 2,2'-azobis(isobutyronitrile) (AIBN, >98%, Tianjin Ruijinte Chemical Company) was purified by recrystallized from ethanol. Other chemical reagents were analytic grade and used as received.

Synthesis of PtBMA by RAFT polymerization. PtBMA was prepared by RAFT polymerization of tBMA in toluene employing CDTPA as RAFT agent and AIBN as initiator under [monomer]$_0$/[RAFT]$_0$/[AIBN]$_0$ = 1200~2800/5/1. Herein, the RAFT polymerization to afford PtBMA$_{329}$, in which the subscript represents the polymerization degree (DP), was typically introduced. Into a Schlenk flask, tBMA (5.972 g, 42.0 mmol), CDTPA (30.3 mg, 0.075 mmol), AIBN (2.46 mg, 0.015 mmol) dissolved in toluene (6.00 g), and the internal standard of 1,3,5-trioxane (0.378 g, 4.20 mmol) for the ^{1}H NMR analysis were added. The solution was initially degassed with nitrogen at 0 °C for 30 min, and then the flask content was immersed into preheated oil bath at 70 °C. After 9 h, the polymerization was quenched by quickly cooling to 0 °C, and the monomer conversion was checked by ^{1}H NMR analysis. The synthesized PtBMA was precipitated into the methanol/water mixture (10/1 by weight) for three times and dried at 40 °C under vacuum. By changing the molar ratio of the tBMA monomer to the RAFT agent as shown in Table 1, the homopolymer of PtBMA with different DP was prepared.

Synthesis of PtBMA-*b*-PVEA by RAFT polymerization. The diblock copolymer of PtBMA-*b*-PVEA was synthesized via RAFT polymerization of VEA in 1,4-dioxane employing the prepared PtBMA as macromolecular RAFT agent (macro-RAFT agent) and AIBN as initiator under [monomer]$_0$/[macro-RAFT]$_0$/[AIBN]$_0$ = 500~2000/3/1. Herein, a typical RAFT polymerization to synthesize PtBMA$_{329}$-*b*-PVEA$_{142}$ was introduced. Into a Schlenk flask, the macro-RAFT agent of PtBMA$_{329}$ ($M_{n,th}$ = 47.2 kg/mol, 1.133 g, 0.024 mmol), VEA (1.514 g, 8.0 mmol), AIBN (1.31 mg, 0.0080 mmol) dissolved in 1,4-dioxane (1.50 g), and 1,3,5-trioxane (72.1 mg, 0.80 mmol) were added. The solution was initially degassed

with nitrogen at 0 °C for 30 min, and then the flask content was immersed into preheated oil bath at 70 °C. After 22 h, the polymerization was quenched by quickly cooling to 0 °C, and the monomer conversion was checked by ^{1}H NMR analysis. The VEA monomer conversion was calculated according to eq 1, in which $I_{5.65-5.80}$ is the integral area of the proton resonance signals at δ = 5.65-5.80 ppm [PhCH=CH_2] corresponding to the remaining VEA monomer and $I_{5.14}$ is the integral area of the proton resonance signals at δ = 5.14 ppm corresponding to the internal standard of 1,3,5-trioxane, respectively. The synthesized diblock copolymer of

PtBMA$_{329}$-b-PVEA$_{142}$ was precipitated in the methanol/water mixture (10/1 by weight) and dried at 40 °C under vacuum. By changing the molar ratio of the VEA monomer to the PtBMA macro-RAFT agent or quenching the polymerization at a predetermined time, the PtBMA-b-PVEA diblock copolymers with different DP of the PtBMA and PVEA blocks as shown in Table 1 were prepared.

$$Conversion\ \% = \frac{5I_{5.14} - 3I_{5.65-5.80}}{5I_{5.14}} \times 100\% \qquad (1)$$

Table 1. Experimental details and summary of PtBMA, PVEA, and PtBMA-b-PVEA.

Entry	Polymer[a]	$[M]_0$:$[CTA]_0$:$[I]_0$	Time (h)	Conv. (%)[b]	$M_{n,th}$[c]	$M_{n,GPC}$[d]	$M_{n,NMR}$[e]	PDI[f]
					M_n (kg/mol)			
A1	B$_{136}$	1200:5:1	7	56.6	19.7	15.0	--	1.16
A2	B$_{217}$	2000:5:1	8	54.2	31.3	27.2	--	1.20
A3	B$_{329}$	2800:5:1	9	58.8	47.2	38.3	--	1.19
B1	A$_{133}$	750:3:1	16	53.1	25.6	14.9	--	1.18
C1	B$_{136}$A$_{138}$	750:3:1	20	55.3	45.9	34.3	45.1	1.19
C2	B$_{217}$A$_{88}$	500:3:1	14	52.6	48.0	38.0	48.1	1.10
C3	B$_{217}$A$_{136}$	800:3:1	22	50.7	57.0	43.6	55.5	1.12
C4	B$_{217}$A$_{184}$	1350:3:1	24	40.9	66.1	48.5	62.7	1.24
C5	B$_{217}$A$_{244}$	2000:3:1	24	36.6	77.4	52.3	74.0	1.30
C6	B$_{329}$A$_{142}$	1000:3:1	22	42.5	74.1	54.8	72.0	1.14

[a] B represents the PtBMA block and A represents the PVEA block; [b] The monomer conversion determined by ^{1}H NMR analysis;[c] Theoretical molecular weight determined by monomer conversion; [d] The molecular weight determined by GPC analysis; [e]The molecular weight determined by ^{1}H NMR analysis; [f] The PDI (M_w/M_n) value determined by GPC analysis.

Characterization. The molecular weight and the polydispersity index (PDI, PDI = M_w/M_n) of the synthesized polymers were determined by a Waters 600E gel permeation chromatography (GPC) equipped with three TSK-GEL columns and a Waters 2414 refractive index detector, where THF containing 3 wt% triethylamine was used as eluent at flow rate of 0.60 mL/min at 30.0 °C and the narrow-polydispersity polystyrene was used as calibration standard. The ^{1}H NMR analysis was performed on a Bruker Avance III 400 MHz NMR spectrometer using CDCl$_3$ as solvent. The differential scanning calorimetry (DSC) analysis was performed on a NETZSCH DSC 204 differential scanning calorimeter under nitrogen atmosphere, in which the sample was heated to 150 °C at the heating rate of 10 °C/min, cooled to 0 °C in 5 min, and then heated to 150 °C at the heating rate of 10 °C/min. The UCST and LCST of the thermo-responsive polymers were determined by turbidity measurement at 500 nm on a Varian 100 UV-vis spectrophotometer equipped with a thermoregulator (± 0.1 °C) with the heating/cooling rate at 1 °C/min. The UCST and LCST values were determined at the middle point of the transmittance change. Dynamic light scattering (DLS) analysis was performed on Nano-ZS90 (Malvern) laser light scattering spectrometer with He-Ne laser at the wavelength of 633 nm at 90° angle, in which the hydrodynamic diameter D_h was determined by intensity following the CONTIN method. The TEM observation was performed on a Tecnai G2 F20 electron microscope at an acceleration of 200 kV, whereby a small drop of the dispersion of the diblock copolymer at a given temperature was dripped onto a piece of preheated/precooled copper grid till the solvent was evaporated.

Results and discussion

### Synthesis of PtBMA and PtBMA-b-PVEA

The PtBMA polymer was synthesized via RAFT polymerization of tBMA in toluene using CDTPA as RAFT agent and AIBN as initiator (Scheme 1). By varying the molar ratio of the monomer to the RAFT agent (tBMA/CDTPA), three polymers of PtBMA$_{136}$, PtBMA$_{217}$, and PtBMA$_{329}$ with the theoretical molecular weight ($M_{n,th}$) at 19.7, 31.3, and 47.2 kg/mol and with the theoretical polymerization degree (DP) at 136, 217, and 329, in which $M_{n,th}$ is calculated by the monomer conversion according to eq 2, were synthesized at around 55-60% monomer conversion (Entries A1-A3, Table 1). Fig. 1 shows the GPC traces of the typical PtBMA$_{329}$, from which the symmetrical and unimodal GPC traces are indicated, and the molecular weight $M_{n,GPC}$ and PDI are obtained. The $M_{n,GPC}$ values by GPC analysis are lower than $M_{n,th}$ by the monomer conversion, and the reason is possibly due to the polystyrene standard employed in the GPC analysis. The PDI values of the synthesized PtBMA locate at 1.16~1.20, suggesting good control in the RAFT polymerization. Fig. 2A shows the ^{1}H NMR spectra of the typical PtBMA$_{329}$, in which the characteristic proton chemical shifts of the PtBMA main chains are clearly observed. However, the chemical shift corresponding to the RAFT terminal is overlapped with those of the polymer backbone or the RAFT terminal signals is too weak, and therefore the polymer molecular weight cannot be accurately estimated by ^{1}H NMR analysis.

$$M_{n,th} = \frac{[monomer]_0 \times M_{monomer}}{[RAFT]_0} \times conversion + M_{RAFT} \qquad (2)$$
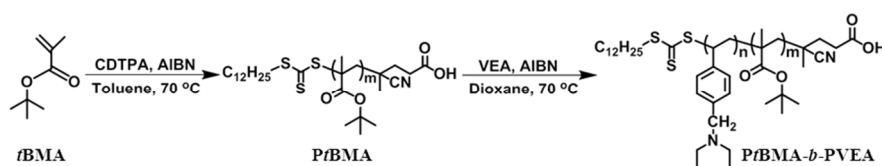
Scheme 1. The schematic synthesis of P*t*BMA and P*t*BMA-*b*-PVEA.
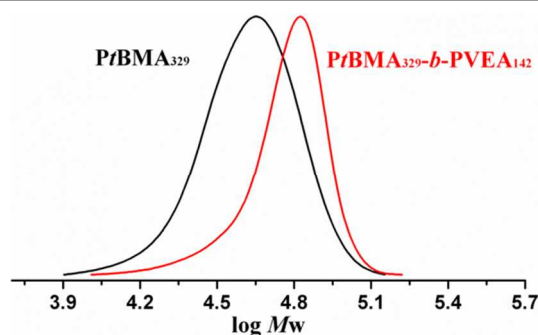
Fig. 1. The GPC traces of the typical P*t*BMA$_{329}$ macro-RAFT agent and the P*t*BMA$_{329}$-*b*-PVEA$_{142}$ diblock copolymer.
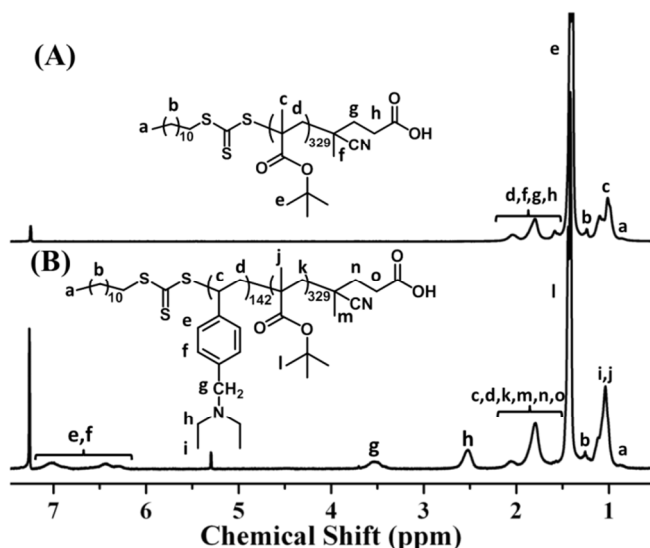
Fig. 2. The ^{1}H NMR spectra of P*t*BMA$_{329}$ (A) and P*t*BMA$_{329}$-*b*-PVEA$_{142}$ (B).

The P*t*BMA-*b*-PVEA diblock copolymers were prepared by sequential RAFT polymerization using P*t*BMA as macro-RAFT agent (Scheme 1). Six diblock copolymers of P*t*BMA$_{136}$-*b*-PVEA$_{138}$, P*t*BMA$_{217}$-*b*-PVEA$_{88}$, P*t*BMA$_{217}$-*b*-PVEA$_{136}$, P*t*BMA$_{217}$-*b*-PVEA$_{184}$, P*t*BMA$_{217}$-*b*-PVEA$_{244}$, and P*t*BMA$_{329}$-*b*-PVEA$_{142}$ were synthesized. The P*t*BMA-*b*-PVEA diblock copolymers were characterized by GPC analysis (Fig. 1) and ^{1}H NMR analysis (Fig. 2), and the results were summarized in Table 1 (Entries C1-C6). It is found that the molecular weight ($M_{n,GPC}$) of the P*t*BMA-*b*-PVEA diblock copolymers by GPC analysis is smaller than the theoretical molecular weight ($M_{n,th}$) calculated by the monomer conversion according to eq 2, and the molecular weight of $M_{n,NMR}$ determined by ^{1}H NMR analysis, which is calculated by comparing the signal at $\delta = 1.36$ ppm

$[COO(CH_3)_3]$ corresponding to the P*t*BMA block to the signal at $\delta = 2.47$ ppm $[PhCH_2N(CH_2CH_3)_2]$ corresponding to the PVEA block, is close to $M_{n,th}$ of the P*t*BMA-*b*-PVEA diblock copolymers The underestimated $M_{n,GPC}$ of the P*t*BMA-*b*-PVEA diblock copolymers by GPC analysis is possibly due to the adsorption of the nitrogen-containing diblock copolymer onto the GPC columns, although the eluent of THF containing 3 wt% triethylamine is used as discussed elsewhere.[69] The synthesized P*t*BMA-*b*-PVEA diblock copolymers have a narrow molecular weight distribution with PDI values at 1.1-1.2, except that of P*t*BMA$_{217}$-*b*-PVEA$_{244}$ containing the longest PVEA block synthesized at the highest ratio of $[monomer]_0/[macro-RAFT]_0/[AIBN]_0$.
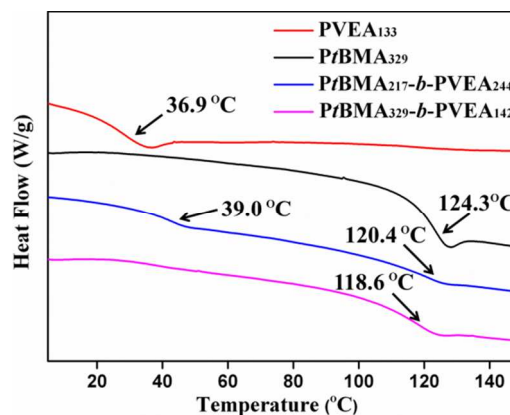
Fig. 3. The DSC thermograms of P*t*BMA$_{329}$, PVEA$_{133}$, P*t*BMA$_{217}$-*b*-PVEA$_{244}$, and P*t*BMA$_{329}$-*b*-PVEA$_{142}$.

The P*t*BMA-*b*-PVEA diblock copolymers were further characterized by DSC analysis. Fig. 3 shows the DSC thermograms of the diblock copolymers of P*t*BMA$_{217}$-*b*-PVEA$_{244}$ and P*t*BMA$_{329}$-*b*-PVEA$_{142}$ and the reference homopolymers of P*t*BMA$_{329}$ and PVEA$_{133}$ (seeing Entry B1 in Table 1 and Fig. S2/S3 in Supporting Information), in which P*t*BMA$_{217}$-*b*-PVEA$_{244}$ exhibits two separate glass transition temperature (T_g) at 39.0 °C corresponding to the PVEA block and at 120.4 °C corresponding to the P*t*BMA block. It is found that T_g of the PVEA block is higher than that of the reference PVEA$_{133}$ homopolymer (36.9 °C) and T_g of the P*t*BMA block is slightly lower than that of the reference P*t*BMA$_{329}$ homopolymer (124.3 °C). However, different from the P*t*BMA$_{217}$-*b*-PVEA$_{244}$ diblock copolymer, P*t*BMA$_{329}$-*b*-PVEA$_{142}$ shows only one T_g at 118.6 °C corresponding to the P*t*BMA block, possibly due to the low percent of the PVEA block in P*t*BMA$_{329}$-*b*-PVEA$_{142}$.

Doubly thermo-responsive schizophrenic behavior of P*t*BMA-*b*-PVEA

Before investigating the thermo-response of the P*t*BMA-*b*-PVEA diblock copolymer, the solubility of the reference homopolymers of P*t*BMA$_{329}$ and PVEA$_{133}$ in methanol is initially checked. In a recent study, the thermo-responsive PVEA showing DP-dependent LCST in methanol was demonstrated.[65] The present PVEA$_{133}$, which contains a RAFT terminal different from those in the previous study,[65] exhibits LCST at 40.0 °C in methanol as shown in Fig. 4A. The soluble-to-insoluble transition of PVEA$_{133}$ in methanol occurs within a very narrow temperature range of 40±1 °C, and little or no hysteresis between the cooling and heating process is observed. As known, poly(methyl methacrylate) (PMMA) is insoluble in methanol and becomes somewhat soluble in ethanol at enhanced temperature.[19,20] However, research on the insoluble-to-soluble phase transition of polymethacrylates or polyacrylates in alcohol at UCST is very precious.[21,70,71] In this study, it is found that P*t*BMA$_{329}$ exhibits a very sharp insoluble-to-soluble phase transition in methanol at UCST of 35.0 °C, and little or no hysteresis between the cooling and heating process is observed (Fig. 4A). As similarly as the general UCST-type polymers,[21,22,65,66,72] the UCST of P*t*BMA in methanol is positively dependent with the polymer molecular weight or polymer DP (Fig. S4). For example, when DP of P*t*BMA increases from 136 to 329, the UCST increases from 16.5 to 35.0 °C.
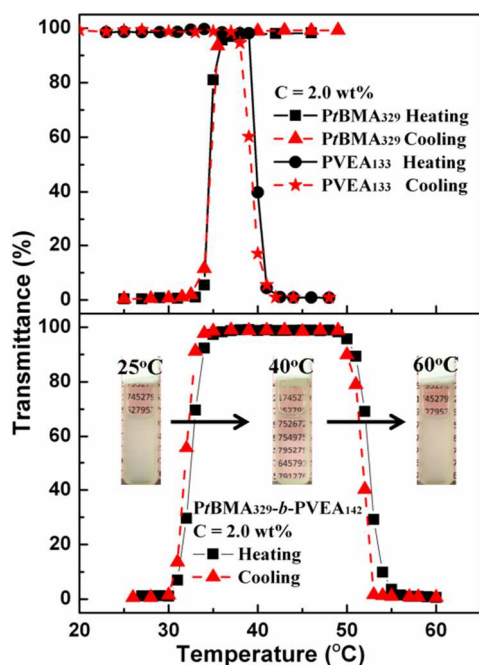

Fig. 4. The transmittance *versus* temperature plots for reference homopolymers of P*t*BMA$_{329}$ and PVEA$_{133}$ (A), and the diblock copolymer of P*t*BMA$_{329}$-*b*-PVEA$_{142}$ (B) in methanol during the heating or cooling process, in which the polymer concentration is 2.0 wt%. The Figure inset shows the digital photographs of P*t*BMA$_{329}$-*b*-PVEA$_{142}$ in methanol taken at different temperature.

With the solubility of the reference homopolymers of P*t*BMA$_{329}$ and PVEA$_{133}$ in hand, the thermo-response of the

P*t*BMA$_{329}$-*b*-PVEA$_{142}$ diblock copolymer containing a LCST-type PVEA block and a UCST-type P*t*BMA in methanol is investigated. As shown in Fig. 4B, P*t*BMA$_{329}$-*b*-PVEA$_{142}$ is molecularly soluble in methanol at temperature ranging from 35 to 51 °C, which is confirmed by the ~ 100 % transmittance and the transparent solution indicated by the insets, from which the digits located at the offside of the UV-vis cell are clearly visible (Seeing the high-resolution digital photographs in Fig. S5). Either increasing temperature above 53 °C or decreasing temperature below 32 °C leads to milky dispersion of the P*t*BMA$_{329}$-*b*-PVEA$_{142}$ diblock copolymer, suggesting the schizophrenic thermo-responsive behavior of the diblock copolymer. According to the solubility of the reference homopolymers of P*t*BMA and PVEA in methanol, it is concluded that the transparent-to-milky transition of P*t*BMA$_{329}$-*b*-PVEA$_{142}$ is due to the soluble-to-insoluble phase transition of the P*t*BMA$_{329}$ block at UCST of 32.0 °C, and the transparent-to-milky transition is due to the soluble-to-insoluble phase transition of the PVEA$_{142}$ block at LCST of 53.0 °C, respectively. The UCST of the P*t*BMA$_{329}$-*b*-PVEA$_{142}$ diblock copolymer (32.0 °C) is lower than that of the reference P*t*BMA$_{329}$ homopolymer (35.0 °C), while its LCST (53.0 °C) is much higher than that of the reference PVEA$_{133}$ homopolymer (40.0 °C), suggesting that the solvophilic block increases the solubility of the thermo-responsive block, which is as similarly as discussed elsewhere.[65-67,73-76] The schizophrenic thermo-response of the diblock copolymer of P*t*BMA$_{329}$-*b*-PVEA$_{142}$ is reversible, and just very slight hysteresis in the cooling/heating process is observed.

In the precious manuscript,[65] it was demonstrated that that the LCST of PVEA decreased with the increase in the polymer concentration. At case of the present P*t*BMA$_{329}$-*b*-PVEA$_{142}$ diblock copolymer, it is found that the LCST corresponding to the PVEA$_{142}$ block decreases with the increase in the polymer concentration and the UCST corresponding to the P*t*BMA$_{329}$ block increases with the increase in the polymer concentration (Fig. S6).
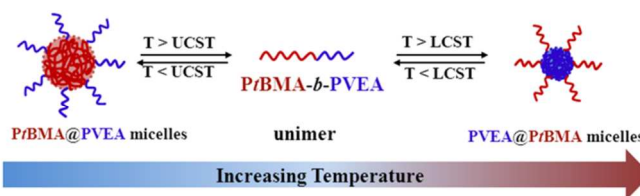

Fig. 5. Schematic representation of the schizophrenic thermo-response of P*t*BMA$_{329}$-*b*-PVEA$_{142}$ in methanol.

Based on the schizophrenic thermo-response of P*t*BMA$_{329}$-*b*-PVEA$_{142}$ in methanol, it is expected that P*t*BMA$_{329}$-*b*-PVEA$_{142}$ forms core-corona micelles with the P*t*BMA as core and PVEA as corona (P*t*BMA@PVEA micelles) at temperature below the UCST of the P*t*BMA$_{329}$ block, and is molecularly soluble (unimer) at temperature above UCST of the P*t*BMA$_{329}$ block while below the LCST of the PVEA$_{142}$ block, and forms core-corona micelles with the PVEA as core and P*t*BMA as corona (PVEA@P*t*BMA micelles) at temperature

above the LCST of the PVEA$_{142}$ block, respectively, as shown in Fig. 5. This schizophrenic thermo-response of PtBMA$_{329}$-b-PVEA$_{142}$ in methanol undergoing micelle-unimer-inverse micelle transformation is confirmed by DLS analysis and TEM observation. To be suitable for DLS analysis, the 0.50 wt% PtBMA$_{329}$-b-PVEA$_{142}$ diblock copolymer solution more diluted than that in the turbidity analysis was employed. As shown in Fig. 6, the average hydrodynamic diameter D_h at 53 nm corresponding to the PtBMA@PVEA micelles formed at 5 ^{0}C below the UCST of the PtBMA$_{329}$ block, D_h at 8 nm corresponding to the unimer or the single soluble diblock copolymer at 40 ^{0}C, and D_h at 42 nm corresponding to the PVEA@PtBMA micelles formed at 60 ^{0}C above the LCST of the PVEA$_{142}$ block are detected, respectively. Note: the apparent hydrodynamic diameter D_h^{app} is afforded herein and the real value may be slightly larger than D_h^{app}. Fig. 7A and 7B show the TEM images of the PtBMA@PVEA micelles and the PVEA@PtBMA micelles, in which nanoparticles with the average size at 29 nm and 18 nm are observed. The D_h values of the schizophrenic diblock copolymer micelles in the present study are larger than those by the TEM observation, and the reason is possibly due to the TEM observation showing the dried aggregates while the DLS analysis detecting the solvated micelles.
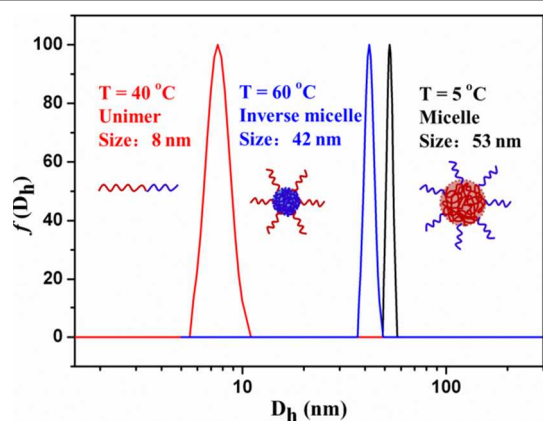

Fig. 6. The hydrodynamic diameter distribution $f(D_h)$ of PtBMA$_{329}$-b-PVEA$_{142}$ at different temperature, in which the polymer concentration is 0.50 wt%.
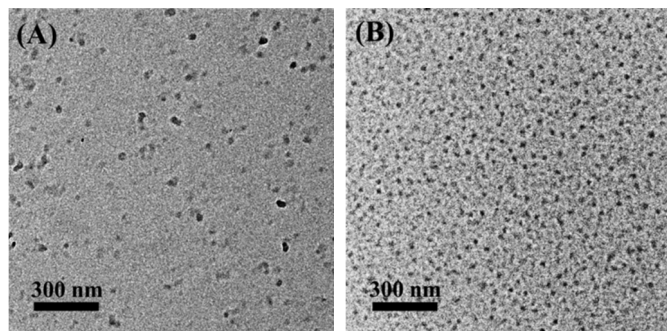

Fig. 7. The TEM images of the PtBMA@PVEA micelles formed at 5 °C below the UCST of the PtBMA$_{329}$ block (A), and the PVEA@PtBMA micelles of the PtBMA$_{329}$-b-PVEA$_{142}$ diblock copolymer formed at 60 °C above the LCST of the PVEA$_{142}$ block (B).

The polymer concentration effect on the micellization of the PtBMA$_{329}$-b-PVEA$_{142}$ schizophrenic diblock copolymer is checked. It is found that the polymer concentration just exerts very slight or no influence on the hydrodynamic diameter D_h of the PtBMA@PVEA micelles and the PVEA@PtBMA micelles (Fig. S7). Note: herein to make comparison and to be suitable for DLS analysis, the present PtBMA@PVEA micelles and the PVEA@PtBMA micelles were prepared by dispersing the diblock copolymer in methanol at a given temperature (5 or 60 °C) and then diluted by preheated/precooled methanol at a similar polymer concentration around 0.50 wt%, and lastly checked by DLS analysis.

Attempt to check the schizophrenic micellization of the PtBMA$_{329}$-b-PVEA$_{142}$ schizophrenic diblock copolymer in deuterated methanol-d_4 (CD$_3$OD) by ^{1}H NMR analysis is made, and however the schizophrenic micellization in deuterated methanol-d_4 (CD$_3$OD) isn't detected. It is found that PtBMA$_{329}$-b-PVEA$_{142}$ can not be molecularly soluble in CD$_3$OD at the temperature from 0 ^{0}C to the boiling point of CD$_3$OD, even much diluted polymer concentration at 0.20 wt% is checked. In the previous manuscript,[65] it was found that the LCST of PVEA in CD$_3$OD was much lower that in CH$_3$OH (methanol). In the present study, it is found that the LCST of the reference PVEA$_{133}$ homopolymer in CD$_3$OD is much lower than that in CH$_3$OH (24 °C vs 40 °C), and the UCST of the reference PtBMA$_{329}$ homopolymer in CD$_3$OD is much higher than in CH$_3$OH (44 °C vs 35°C) (seeing detail in Fig. S8). The UCST increasing and the LCST decreasing leads to the UCST becoming higher than LCST, and therefore leads to BMA$_{329}$-b-PVEA$_{142}$ being insoluble in CD$_3$OD. The micellization of PtBMA$_{329}$-b-PVEA$_{142}$ in CD$_3$OD may be interesting, and however it is not focused in the present study.

Effect of block length on the thermo-responsive behavior of PtBMA-b-PVEA

The effect of the block chain length on the thermo-responsive behavior of the PtBMA-b-PVEA diblock copolymer is further investigated. To fulfill this investigation, six well-defined diblock copolymers of PtBMA$_{136}$-b-PVEA$_{138}$, PtBMA$_{217}$-b-PVEA$_{88}$, PtBMA$_{217}$-b-PVEA$_{136}$, PtBMA$_{217}$-b-PVEA$_{184}$, PtBMA$_{217}$-b-PVEA$_{244}$, and PtBMA$_{329}$-b-PVEA$_{142}$ as shown in Table 1 are synthesized. Clearly, these six diblock copolymers can be classified in two groups. In the first group of PtBMA$_{136}$-b-PVEA$_{138}$, PtBMA$_{217}$-b-PVEA$_{136}$, and PtBMA$_{329}$-b-PVEA$_{142}$ (Group 1), the DP of the PVEA block is similar with each other while the DP of the PtBMA block increases from 136 to 329. In the second group of PtBMA$_{217}$-b-PVEA$_{88}$, PtBMA$_{217}$-b-PVEA$_{136}$, PtBMA$_{217}$-b-PVEA$_{184}$, and PtBMA$_{217}$-b-PVEA$_{244}$ (Group 2), the DP of the PtBMA block is kept at the constant of 217 while the DP of the PVEA block increases from 88 to 244.

By checking the schizophrenic thermo-response of the Group 1 diblock copolymers with very similar DP of the PVEA block, it is found that the DP of the PtBMA block exerts great influence on both the UCST of the PtBMA block and the LCST of the PVEA block of the PtBMA-b-PVEA diblock copolymers

in methanol. Fig. 8A indicates that the UCST of the PtBMA block increases with its DP for the Group 1 diblock copolymers. For example, the PtBMA$_{136}$-b-PVEA$_{138}$ diblock copolymer containing the shortest PtBMA$_{136}$ block is soluble in methanol even at -10 ^{o}C. Whereas, when the DP of the PtBMA block increases from 217 to 329, the UCST of the PtBMA block increases from 19 to 32 ^{o}C. This result is as similar as the PtBMA homopolymer, whose UCST increases from 16.5 to 35 ^{o}C when the DP increases from 136 to 329 (Fig. S4 in Supporting Information). The reason that the UCST increases with increasing polymer DP is possibly due to the strong polymer-polymer interaction in the high molecular weight polymer as discussed elsewhere.[66,82] As shown in Fig. 8B, the LCST of the PVEA block of the PtBMA-b-PVEA diblock copolymer is higher than that of the PVEA$_{133}$ reference homopolymer (40.0 ^{0}C), and the LCST increases with the increasing DP of the PtBMA block. That is, the LCST of the PVEA block increases from 47.5 to 53.0 ^{o}C, when the DP of the PtBMA block increases from 136 to 329. The reason that the LCST of the PVEA block increases with the increasing DP of the PtBMA block is discussed. At the temperature higher than UCST, the PtBMA block becomes soluble in methanol and therefore is solvophilic. This solvophilic PtBMA block increases the solubility of the PVEA block in methanol, and

therefore the LCST of the PVEA block is increased as similarly as the doubly hydrophilic block copolymers discussed elsewhere.[65-67,73-76]

By comparing the schizophrenic thermo-response of the Group 2 diblock copolymers with the same DP of the PtBMA block, it is found that both the UCST of the PtBMA block and the LCST of the PVEA block decrease with the increasing DP of the PVEA block (Fig. 9). For example, when the DP of the PVEA block increases from 88 to 244, the UCST of the PtBMA$_{217}$ block is lower than that of the reference PtBMA$_{217}$ homopolymer at 27.5 ^{0}C and the UCST decreases from 22 to 12 ^{o}C (Fig. 9A), and the LCST of the PVEA block decreases from above the boiling point (65 ^{o}C) to 40.5 ^{o}C. The reason is discussed. At temperature below the UCST of the PtBMA block, the PVEA block is soluble, which can increases the solubility of the PtBMA block in methanol, and therefore the UCST of the PtBMA block decreases with the increasing DP of the PVEA block. In the previous study,[65] It was found that the LCST of the PVEA homopolymer decreased with the increasing polymer DP, which is just like that in the present study at case of the PtBMA-b-PVEA diblock copolymer. This possibly suggests that PVEA with lower DP have a better solubility in methanol.
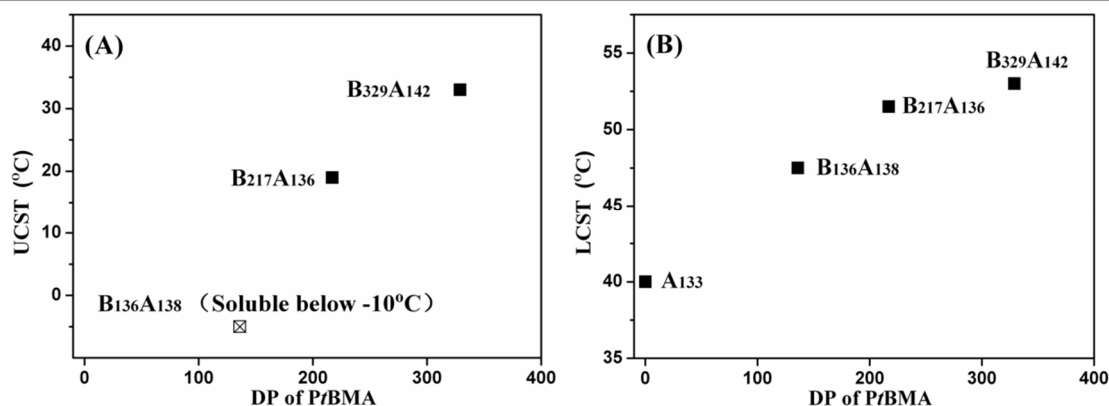

Fig. 8. The effect of block chain length on the UCST and LCST of the Group 1 PtBMA-b-PVEA block copolymers in methanol, in which the polymer concentration is 2.0 wt %. Insets: B represents the PtBMA block and A represents the PVEA block.
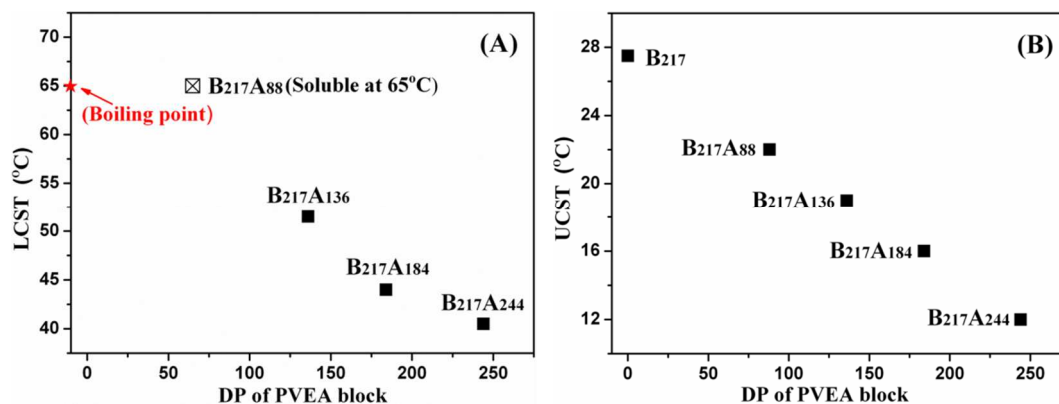

Fig. 9. The effect of block chain length on the UCST and LCST of the Group 2 PtBMA-b-PVEA block copolymer in methanol, in which the polymer concentration is 2.0 wt %. Insets: B represents the PtBMA block and A represents the PVEA block.

The effect of block length on the PtBMA@PVEA micelles formed at 5 °C below the UCST of the PtBMA block and the PVEA@PtBMA micelles formed at 60 °C above the LCST of the PVEA block is checked by TEM observation. As indicated by the TEM images shown in Fig. S9, the average size of the PtBMA@PVEA micelles decreases with the DP of the corona-forming PVEA block, and the DP of the core-forming PVEA block has no or very slight influence of the size of the inverse PVEA@PtBMA micelles. The reason that the size of the PtBMA@PVEA micelles decreases with the DP of the corona-forming PVEA block is possible due to the increasing inherent molecular curvature and the reduced aggregation number of the PtBMA@PVEA micelles, which has been well demonstrated in the micellization of amphiphilic diblock copolymer in block-selective solvents.[66,77-80]

Conclusions

Well-defined doubly thermo-responsive schizophrenic diblock copolymer of PtBMA-b-PVEA containing a UCST-type PtBMA block and a LCST-type PVEA block is prepared by sequential RAFT polymerization. At temperature below the UCST of the PtBMA block, the PtBMA block is solvophobic and the PVEA block is solvophilic in methanol, and PtBMA@PVEA micelles containing a PtBMA core and a PVEA corona are formed. At temperature above the UCST of the PtBMA block and below the LCST of the PVEA block, PtBMA-b-PVEA is molecularly soluble in methanol. At temperature above the LCST of the PVEA block, the PtBMA block is solvophilic and the PVEA block becomes solvophobic, and inverse PVEA@PtBMA micelles containing a PVEA core and a PtBMA corona are formed. The thermo-responsive flip-flop transformation from PtBMA@PVEA micelles to unimer and further to inverse PVEA@PtBMA micelles is perfectly reversible. The DP of the PtBMA block or the PVEA block affecting the UCST of the PtBMA block and the LCST of the PVEA block and the size of the PtBMA@PVEA micelles and inverse PVEA@PtBMA micelles is investigated. It is found that, the UCST of the PtBMA block and the LCST of the PVEA block increase with the increasing DP of the PtBMA block and whereas they decrease with the increasing DP of the PVEA block. The average size of the PtBMA@PVEA micelles decreases with the DP of the corona-forming PVEA block, and the DP of the core-forming PVEA block has nor or very slight influence of the size of the inverse PVEA@PtBMA micelles.

Acknowledgements

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Table of Contents for:

Synthesis of doubly thermo-responsive schizophrenic diblock copolymer based on poly[*N*-(4-vinylbenzyl)-*N,N*-diethylamine] and its temperature-sensitive flip-flop micellization

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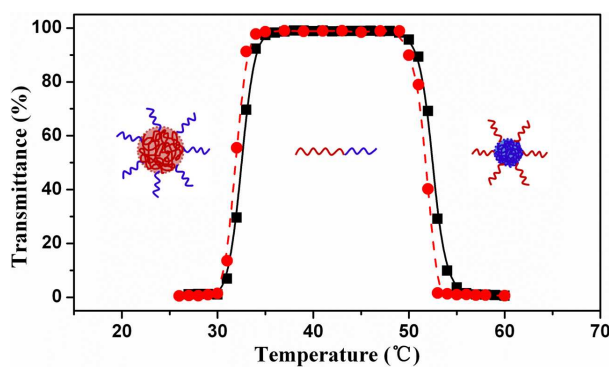
Doubly thermo-responsive schizophrenic diblock copolymer of poly(*tert*-butyl methylacrylate)-*block*-poly[*N*-(4-vinylbenzyl)-*N,N*-diethylamine] was synthesized and its temperature-sensitive flip-flop micellization was demonstrated.