Macromolecules

Versatile Synthesis of Multiarm and Miktoarm Star Polymers with a Branched Core by Combination of Menschutkin Reaction and Controlled Polymerization

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Supporting Information

ABSTRACT: Menschutkin reaction and controlled polymerization were combined to construct three types of star polymers with a branched core. Branched PVD was synthesized by reversible addition—fragmentation chain transfer (RAFT) copolymerization and used as a core reagent to synthesize multiarm and miktoarm stars with poly(ε caprolactone) (PCL), polystyrene, poly(methyl methacrylate), poly(*tert*-butyl acrylate), and poly(*N*-isopropylacrylamide) segments. Effects of reaction time, feed ratio, and arm length on coupling reaction between PVD and bromide-function-



alized polymer were investigated, and a variety of A_m -type stars ($m \approx 7.0-35.1$) were obtained. Meanwhile, $A_m B_n$ stars ($m \approx 9.0$, $n \approx 6.1-11.3$) were achieved by successive Menschutkin reactions, and $A_m C_o$ stars ($m \approx 8.8-9.0$, $o \approx 5.0$) were generated by tandem quaternization and RAFT processes. Molecular weights of various stars usually agreed well with the theoretical values, and their polydispersity indices were in the range of 1.06-1.24. The arm number, chain length, and chemical composition of star polymers could be roughly adjusted by control over reaction conditions and utilization of alternative methods, revealing the generality and versatility of these approaches. These ion-bearing stars were liable to exhibit solubility different from normal covalently bonded polymers, and the chain relaxation and melting behaviors of polymer segments were strongly dependent on the macromolecular architecture.

INTRODUCTION

Synthesis and properties of complex macromolecular architectures such as multiarm and miktoarm stars have attracted much attention in the past decades due to their unique topologies and physicochemical properties.^{1–20} Owing to their compact structure and variable functionality, star polymers usually exhibit bulk, solution, and interface properties different from their linear analogues and have potential applications in many fields.^{21–34} Moreover, miktoarm stars with at least two kinds of polymer arms are liable to form higher order multiscale self-assemblies involving multicompartment micelles originating from their branched architectures and heterophase structures, and thus they can hold great promise as next-generation advanced functional polymers.^{35–46}

To date, some approaches involving "arm first",^{47–52} "core first",^{53–55} and "coupling onto"^{56,57} methods based on linking reactions and living/controlled polymerization techniques have been efficiently used to construct numerous well-defined star polymers although all of them have more or less disadvantages. Generally speaking, the "arm first" approach using cross-linker is liable to afford star polymers with poor structural homogeneity and broadened molecular weight distribution in which the formed core is of rather complex structure, the "core first" approach to generate regular stars usually needs stopping the reaction at suitable conversion to avoid star–star coupling, and the "coupling onto" method sometimes suffers from inefficient coupling reactions between polymer segments and functional core.^{21–27} To further address these limitations, it is necessary to explore new synthetic methodology to construct star polymers, which potentially plays a crucial role in promoting the development of polymer and materials science.

Meanwhile, self-condensing vinyl polymerization (SCVP)⁵⁸ has been extended to controlled radical processes such as nitroxide-mediated polymerization (NMP),^{59,60} atom transfer radical polymerization (ATRP),^{61–65} and reversible addition– fragmentation chain transfer (RAFT) polymerization^{66–75} to prepare hyperbranched polymers with variable molecular parameters. More importantly, part of branched polymers can act as functional initiator or chain transfer agent (CTA) to generate multiarm stars.^{53–55,76–79} For instance, RAFT copolymerization via self-condensing vinyl polymerization (RAFT SCVP) was used by us to synthesize multifunctional branched copolymers and followed by chain extension polymerization to prepare multiarm stars with predetermined arm number and controlled arm length.⁷⁸ More recently, Gao and co-workers have successfully combined RAFT SCVP,

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Received:September 19, 2012Revised:November 6, 2012Published:November 16, 2012
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Scheme 1. Synthetic Routes to Various Multiarm and Miktoarm Stars by Combination of Menschutkin Reaction and Controlled Polymerization



Menschutkin reaction, and Cu(I)-catalyzed azide-alkyne cycloaddition reaction to synthesize hyperbranched macroinitiators, dendritic polymer brushes, and star-shaped polymers.⁷⁹ The Menschutkin reaction between alkyl halide and amine is liable to quantitatively yield a quaternary ammonium salt,⁸⁰ which has been efficiently used to construct ioncontaining linear polymers, conjugated polymers, block copolymers, branched, and dendritic polymers besides its wide application in organic synthesis.^{79,81–86} This S_N^2 reaction offering a facile method to N-C bond formation can be accelerated by polar aprotic solvents, increased temperature and pressure, and enhanced leaving-group ability, in which initial polymer, alkylating agent, and modified polymer had better dissolve in the solvent. To our knowledge, Menschutkin reaction between polymers has been scarcely investigated although it has a great potential in novel architecture construction. Therefore, it is very timely to extend such method to construct functional multiarm and miktoarm stars with controlled compositions and precise microstructures.

The marriage of RAFT SCVP and Menschutkin reaction potentially opens an avenue to address the synthetic difficulty of multiarm and multicomponent stars. Herein we report on facile synthesis of three types of novel multiarm and miktoarm stars with a branched core by this combinatorial approach, in which polymeric chains were grafted onto the branched scaffold via Menschutkin reaction to construct complex macromolecular architectures for the first time (Scheme 1). RAFT copolymerization of 4-vinylbenzyl dithiobenzoate (VBDB)⁷⁵ and N_rN - dimethylaminoethyl methacrylate (DMA) was first performed to generate branched poly(VBDB-co-DMA) (abbreviated as PVD) with reactive dithiobenzoate moieties, couplable tertiary amino groups, and relatively low polydispersity indices. On this basis, A_m - and $A_m B_n$ -type stars (in which the subscript meant the average number of arms) were obtained by Menschutkin reaction(s) between branched PVD and as-prepared bromideterminated polymers, and A_mC_o-type miktoarm stars were generated by tandem quaternization process and RAFT polymerization. The isolated stars and their precursors were characterized by ¹H and ¹³C NMR, GPC, GPC-MALLS, IR, and DSC. These approaches allow for versatile synthesis of the target ion-bearing stars with tunable chemical composition, well-defined arm length, and roughly controlled number of arms due to relatively high grafting efficiency and mild reaction conditions.

EXPERIMENTAL SECTION

Materials. All solvents, monomers, and other chemicals were purchased from Sigma-Aldrich unless otherwise stated. Methyl methacrylate (MMA, 99%), *tert*-butyl acrylate (*t*BA, 98%), *N*,*N*dimethylaminoethyl methacrylate (DMA, 99%), and styrene (St, 99%) were passed through a basic alumina column to remove the inhibitor, and ε -caprolactone (CL, 99%) was distilled over CaH₂ under reduced pressure before use. *N*-Isopropylacrylamide (NIPAM, 97%) was recrystallized twice from mixtures of hexane and toluene. 2,2'-Azobis(isobutyronitrile) (AIBN, 99%) was recrystallized twice from ethanol. Dichloromethane (DCM) and dioxane were dried and distilled over CaH₂, toluene was distilled over sodium and

Table 1. Results for Synthesis of PVD Branched	Copolymers by RAFT	Copolymerization of V	BDB and DMA in Dioxane at 80
°C ^a			

run	DP ₀	<i>t</i> (h)	C $(\%)^{b}$	$M_{ m n,MALLS}{}^c$	PDI ^c	$RB(th)^d$	RB^{e}	P_1^f	F_n^{g}	$F_{\rm w}^{\ g}$
1	5	12	71.6	23 000	4.96	4.58	6.54	0.30	27.4	136
2	10	12	66.3	41 600	4.86	7.63	9.78	0.22	31.7	154
3	30	12	72.4	57 500	3.24	22.7	31.5	0.28	15.6	50.6
4	20	20	46.2	8 630	1.32	10.2	12.0	0.20	5.0	6.6
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^{*a*}Polymerization conditions: $[DMA]_0$: $[VBDB]_0$: $[AIBN]_0 = DP_0$: 1:0.2, $[DMA]_0 = 3.0 \text{ mol/L} (\text{runs } 1-3)$; $[DMA]_0$: $[VBDB]_0$: $[AIBN]_0 = DP_0$: 1:0.1, $[DMA]_0 = 0.60 \text{ mol/L} (\text{run } 4)$. ^{*b*}DMA conversion determined by ¹H NMR. ^{*c*}Number-average molecular weight and polydispersity determined by GPC-MALLS. ^{*d*}Theoretical repeat units per branch calculated by equation RB(th) = $DP_0 \times C\% + 1$. ^{*e*}Repeat units per branch determined by ¹H NMR, RB = $(I_{7.98} + I_{4.06})/(I_{7.98} - I_{4.53})$, where *I* meant peak area at various chemical shifts. ^{*f*}Proportion of dithiobenzoate functionality connecting with benzyl moiety. ^{*g*}Number-average (*F*_n) and weight-average (*F*_w) CTA functionalities per branched copolymer.

benzophenone, and *N*,*N*-dimethylformamide (DMF) was dried over MgSO₄ and distilled under reduced pressure. 4-Vinylbenzyl chloride (90%) and tin(II) 2-ethylhexanoate (Sn(Oct)₂, 95%) were used as received. *N*,*N*'-Dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), and other chemicals with analytical grade were purchased from Sinopharm Chemical Reagent and used as received. 4-Vinylbenzyl dithiobenzoate (VBDB),⁷⁵ 4-cyanopentanoic acid-4-dithiobenzoate (4-CPDB),⁸⁷ and *S*-(4-trimethoxysilyl)benzyl *S*'-propyltrithiocarbonate (TBPT)⁸⁸ were synthesized and purified according to literature methods. Silica gel (Qingdao Haiyang Chemical Co., Ltd.) had an average particle size of 10 μ m, BET specific surface area of 297.1 m²/g, and average pore size of 11.5 nm.

Synthesis of 3-Bromopropyl 4-(Benzodithioyl)-4-cyanopentanoate (BBCP). To a round flask were added 3-bromo-1-propanol (1.53 g, 11.0 mmol), 4-CPDB (2.80 g, 10.0 mmol), DMAP (0.122 g, 1.0 mmol), and dry DCM (50 mL), and then 20 mL of DCM solution containing 2.50 g (12.1 mmol) of DCC was slowly added to the above solution cooled with ice-water bath under nitrogen. The contents were further stirred at ambient temperature for 18 h. After filtration, the filtrate was partitioned between water and DCM, and the aqueous layer was extracted twice with DCM. The combined extracts were dried over MgSO4 overnight. The crude product was purified by flash column chromatography eluting with hexane/DCM (1:1, v/v), and 3.76 g (93.9% yield) of BBCP was obtained. ¹H NMR (CDCl₃): δ 7.90 (d, J 8.4, PhH, 2H), 7.57 (t, J 6.8, PhH, 1H), 7.40 (t, J 9.6, PhH, 2H), 4.27 (t, J 7.6, CH₂O, 2H), 3.47 (t, J 8.4, CH₂Br, 2H), 2.67 (m, CH₂, 2H), 2.60 and 2.44 (m, CH2, each 1H), 2.20 (m, CH2, 2H), 1.94 (s, CH₃, 3H). ¹³C NMR (CDCl₃): δ 222.1 (C=S), 171.2 (C=O), 144.2, 132.9, 128.4, 126.5 (PhC), 118.3 (CN), 62.6 (CH₂O), 45.5 (CH₃CCN), 33.1, 31.3, 29.5, 29.3 (CH₂), 23.9 (CH₃). FT-IR (KBr): 3455, 3078, 3058, 3028, 2962, 2932, 2856, 2230, 1739, 1590, 1513, 1483, 1445, 1421, 1393, 1293, 1233, 1183, 1108, 1081, 1046, 1026, 999, 926, 868, 762, 688, 650, 617, 576 cm⁻¹. Elem. Anal. Calcd for C₁₆H₁₈BrNO₂S₂: C, 48.00%; H, 4.53%; N, 3.50%; S, 16.02%. Found: C, 48.12%; H, 4.55%; N, 3.48%; S, 15.96%.

Synthesis of Hyperbranched Copolymers by RAFT Copolymerization of VBDB with DMA. In a typical experiment (run 4 of Table 1), DMA (15.7 g, 100 mmol), VBDB (1.35 g, 5.0 mmol), AIBN (82 mg, 0.5 mmol), and 150 mL of dioxane were added to a round flask with a magnetic stirring bar, and the contents were degassed with bubbled nitrogen for 1 h. The polymerization was performed at 80 °C for 20 h, and DMA conversion was determined to be 46.2% by ¹H NMR analysis. The polymerization solution was concentrated and precipitated into cold hexane thrice, and 8.35 g of branched PVD was obtained. Number-average molecular weight and polydispersity determined by GPC-MALLS were $M_{n,MALLS} = 8630$ and PDI = 1.32. Other branched copolymers were synthesized and isolated according to a similar approach. ¹H NMR (CDCl₃): δ 7.98 (PhH), 6.7–7.7 (PhH and ArH), 5.0-5.5 (CHS), 4.53 (CH₂S), 4.24 (CH₂O, terminal DMA unit), 4.06 (CH2O, DMA unit), 3.30 (CH2, terminal DMA unit), 2.57 (CH₂N, DMA unit), 2.28 ((CH₃)₂N, DMA unit), 0.5-2.2 (CH, CH₂ and CH₃). ¹³C NMR (DMSO- d_6): δ 222.7 (C=S), 176.8, 176.5, 175.8 (C=O), 145.0, 144.4, 136.2, 135.0, 133.9, 130.7, 129.1, 128.9, 128.2, 126.7 (ArC and PhC), 62.4 (CH₂O of DMA unit), 56.6 (CH₂N of DMA unit), 53.6 (CH₂ of DMA unit), 45.1 (CH₃N of DMA

unit), 44.5 (CH₂S, CHS and CH₃CS), 44.2 (CH₃CCOO of DMA unit), 25.9–37.4 (CH₂), 18.2, 16.4 (CH₃ of DMA unit). FT-IR (KBr): 3431, 2947, 2860, 2821, 2770, 1730, 1655, 1638, 1560, 1542, 1508, 1459, 1400, 1364, 1272, 1150, 1100, 1058, 1042, 1017, 965, 853, 779, 748, 689 cm⁻¹.

Synthesis of PDMA Grafted Silica Particles. To a round flask were added S-(4-trimethoxysilyl)benzyl S'-propyltrithiocarbonate (TBPT, 10.9 g, 30 mmol), silica particles (15.0 g), and dry toluene (150 mL), and the mixture was stirred at 85 °C overnight. After filtration, the crude product was thoroughly washed with THF (100 mL \times 3), toluene (100 mL \times 3), and acetone (100 mL \times 2). After vacuum drying, TBPT tethered silica (Si-TBPT, 17.5 g) was obtained as a yellow powder. The CTA loading was determined to be 0.541 mmol/g by elemental analysis (based on sulfur content of 5.20%).

Si-TBPT (10.0 g, 5.41 mmol), DMA (51.2 g, 326 mmol), AIBN (0.178 g, 1.09 mmol), and dioxane (100 mL) were added to a 250 mL of round flask under nitrogen. The contents were cooled with ice-water bath and degassed with bubbled nitrogen for 1 h. The RAFT graft polymerization was performed at 60 °C for 20 h. After concentration and precipitation into a large amount of cold hexane, monomer conversion was determined to be 83.2% by gravimetry. The mixture was dispersed into 150 mL of THF and filtered, and crude product was collected and thoroughly washed with THF. After vacuum drying, 14.1 g of SiO₂-g-PDMA was obtained. The weight ratio of grafted PDMA to silica particles determined by TGA was 42.5%, corresponding to 1.68 mmol of DMA unit per g of SiO₂-g-PDMA.

Synthesis of Bromide-Terminated Polymers. In a typical polymerization (run 1 of Table S1), St (10.4 g, 100 mmol), BBCP (0.40 g, 1.0 mmol), and AIBN (33 mg, 0.2 mmol) were added to a Schlenk tube with a magnetic stirring bar, and the contents were degassed with bubbled nitrogen for 20 min. The polymerization was performed at 60 °C for 16 h, and monomer conversion was determined to be 21.6% by ¹H NMR analysis. The polymerization solution was concentrated and precipitated into cold hexane thrice, and 2.55 g of PSt-Br was obtained. Number-average molecular weight and polydispersity estimated by GPC were $M_{n,GPC} = 2370$ and PDI = 1.10. Other bromide-functionalized polymers were synthesized and isolated according to a similar approach, in which PCL-Br was synthesized by CL polymerization initiated with 3-bromo-1-propanol using Sn(Oct)₂ catalyst.

*P*St-Br. ¹H NMR (CDCl₃): δ 6.2–8.0 (PhH), 4.6–5.0 (broad, CH of terminal St unit), 4.17 (CH₂O), 3.42 (CH₂Br), 2.61 (CH₂CH₂CH₂Br), 0.6–2.4 (CH₂CO, CH and CH₂ of PSt). ¹³C NMR (DMSO-*d*₆): δ 222.7 (C=S), 171.8 (C=O), 145.1, 128.6, 128.0, 127.3, 126.5, 125.7 (PhC), 118.2 (CN), 62.1 (BrCH₂CH₂CH₂O), 43.8 (CH₂ of PSt and CHS), 36.5, 35.6, 35.0, 34.3, 33.3, 32.8 (CH of PSt and CH₂CH₂COO), 31.3 (CH₂Br), 31.0 (CH₂CH₂Br), 29.3 (CH₂COO), 23.4 (CH₃), 22.6 (CH₃CCN). FT-IR (KBr): 3082, 3059, 3025, 3003, 2922, 2849, 1943, 1870, 1802, 1740, 1601, 1583, 1493, 1452, 1371, 1180, 1155, 1069, 1045, 1028, 907, 876, 841, 758, 698 cm⁻¹.

PMMA-Br. ¹H NMR (CDCl₃): δ 7.90, 7.53, and 7.37 (m, PhH), 4.25 (CH₂O), 3.60 (CH₃O of PMMA), 3.40 (CH₂Br), 2.51 (CH₂CH₂CH₂Br), 2.20 (CH₂CO), 0.5–2.1 (CH₂ and CH₃ of

Table 2. Results for Synthesis of Multiarm A_m -Type Stars with a Branched Core by Menschutkin Reaction between PVD and PM-Br^{*a*}

run	arm ^b	r_0^c	<i>t</i> (h)	$Y(\%)^d$	$M_{ m n,th}^{e}$	$M_{\mathrm{n,MALLS}}f$	PDI	$M_{\rm n,NMR}^{\ g}$	m^h	CE $(\%)^{i}$
1	PSt _{20.0}	0.80	3.5	23.6	30 200	31 100	1.21	30 800	9.1	24.6
2	PSt _{20.0}	0.80	8	40.2	45 300	46 600	1.23	46 900	15.3	41.6
3	PSt _{20.0}	0.80	20	50.5	54 700	56 900	1.19	56 600	19.5	52.9
4	PSt _{20.0}	0.80	40	59.8	63 200	66 900	1.18	65 300	23.5	63.8
5	PSt _{39.6}	0.80	40	33.5	64 400	63 800	1.20	64 900	12.2	33.2
6	PSt _{56.2}	0.80	40	22.4	60 200	66 300	1.16	64 400	9.2	25.1
7	PSt _{88.3}	0.80	40	19.2	76 500	76 900	1.11	75 200	7.1	19.3
8	PSt _{39.6}	0.20	40	76.8	40 600	40 100	1.24	40 900	7.0	75.7
9	PSt _{39.6}	0.50	40	45.5	55 900	56 200	1.16	53 300	10.5	45.8
10	PSt _{39.6}	1.0	40	28.3	67 500	66 400	1.22	67 200	12.8	27.8
11	PMMA _{34.6}	0.60	40	52.4	64 500	66 800	1.10	66 200	15.1	54.6
12	PtBA36.3	0.80	40	36.6	76 600	81 100	1.13	79 500	14.4	39.0
13	PNIPAM _{23.3}	0.50	40	90.5	71 700	76 500	1.24	75 600	22.4	97.4
14	PCL _{13.6}	0.20	40	95.6	23 500	23 800	1.11	23 900	9.0	97.6
15	PCL ₁₃₆	0.80	40	92.8	66 300	67 900	1.20	69 300	35.1	95.3

^{*a*}Reaction conditions: $W_{polymer}$: $V_{DMF} = 0.20 \text{ g/mL}$, in DMF at 60 °C. ^{*b*}The subscript denoted polymerization degree of PM-Br determined by ¹H NMR. ^{*c*}Molar ratio of PM-Br to DMA unit of PVD. ^{*d*}Yield of isolated star polymer. ^{*e*}Theoretical molecular weight, $M_{n,th} = M_{n,PVD} + 46M_{n,arm} \times \text{yield}$, in which 46 was average number of DMA unit per branched PVD, and $M_{n,PVD}$ and $M_{n,arm}$ were molecular weights of PVD and PM-Br. ^{*f*}Number-average molecular weight and polydispersity of star polymer determined by GPC-MALLS. ^{*g*}Number-average molecular weight determined by ¹H NMR. ^{*h*}Average arm number of PM segments grafted onto the surface of PVD. ^{*i*}Coupling efficiency of Menschutkin reaction.

PMMA). FT-IR (KBr): 2996, 2951, 2844, 1732, 1485, 1449, 1387, 1272, 1242, 1193, 1149, 1063, 988, 966, 912, 842, 810, 750, 695 cm⁻¹.

PtBA-Br. ¹H NMR (CDCl₃): δ 7.97, 7.53, and 7.38 (m, PhH), 4.64 (CH of terminal *t*BA unit), 4.24 (CH₂O), 3.47 (CH₂Br), 2.51 (CH₂CH₂CH₂CH₂Br), 2.23 (CH of PtBA and CH₂CO), 0.5–2.0 (CH₂ and CH₃ of PtBA). FT-IR (KBr): 2979, 2934, 2876, 1728, 1481, 1458, 1394, 1368, 1258, 1147, 1033, 909, 846, 753, 689 cm⁻¹.

PNIPAM-Br. ¹H NMR (CDCl₃): δ 7.97, 7.58, and 7.41 (m, PhH), 6.0–7.2 (broad, NH of PNIPAM), 4.24 (CH₂O), 4.01 (CH of PNIPAM), 3.47 (CH₂Br), 2.80 (CHCO of PNIPAM), 2.50 (CH₂CH₂CH₂CH₂Br), 0.5–2.4 (CH₂CO, CH₂ and CH₃ of PNIPAM). FT-IR (KBr): 3432, 3300, 3074, 2973, 2934, 2876, 1725, 1652, 1545, 1459, 1387, 1368, 1326, 1275, 1236, 1173, 1131, 1047, 984, 927, 880, 840, 764, 688 cm⁻¹.

PCL-Br. ¹H NMR (CDCl₃): δ 4.24 (t, *J* 5.1, BrCH₂CH₂CH₂O), 4.06 (s, CH₂O of PCL), 3.65 (t, *J* 6.3, CH₂OH), 3.47 (t, *J* 6.3, CH₂Br), 2.31 (s, CH₂CO of PCL), 2.18 (t, *J* 6.0, BrCH₂CH₂CH₂O), 1.65 (m, CH₂CH₂CH₂CH₂CH₂CH₂O of PCL), 1.38 (m, CH₂CH₂CH₂CH₂CH₂CH₂O of PCL), 1.38 (m, CH₂CH₂CH₂CH₂CH₂CH₂O of PCL), 1.38 (m, CH₂CH₂CH₂CH₂CH₂O) of PCL), 61.8 (BrCH₂CH₂CH₂O), 60.6 (CH₂OH), 33.4 (CH₂COO of PCL), 32.3 (CH₂CH₂OH), 31.3 (CH₂Br), 30.9 (CH₂CH₂Br), 27.9 (CH₂CH₂CH₂CH₂CH), 24.2 (CH₂CH₂CH₂CO of PCL), 24.5 (CH₂CH₂CH), 24.5 (2CH₂OH), 24.5 (2CH₂OH), 24.5 (2CH₂OH), 24.5 (2CH₂CH₂OH), 24.5 (2CH₂CH₂OH), 24.5 (2CH₂CH₂OH), 24.5 (2CH₂OH), 24.5 (2CH₂CH₂OH), 24.5 (2CH₂CH₂OH), 24.5 (2CH₂CH₂OH), 24.5 (2CH₂CH₂OH), 24.5 (2CH₂CH₂CH₂OH), 24.7 (2CH₂CH₂CH₂OH), 24.7 (2CH₂CH₂CH₂OH), 24.7 (2CH₂CH₂CH₂OH), 24.7 (2CH₂CH₂CH₂CH), 24.7 (2CH₂CH₂CH₂OH), 24.7 (2CH₂CH₂CH₂CH), 24.7 (2CH₂CH₂CH), 24.7 (2CH₂CH), 24.7 (2CH₂CH), 24.7 (2CH₂CH), 24.7 (2CH₂CH), 24.7 (2CH), 24.7 (2C

Synthesis of A_m -Type Multiarm Stars with a Branched Core by Menschutkin Reaction. In a typical experiment (run 4 of Table 2), branched PVD (50 mg, 0.267 mmol DMA unit), PSt-Br ($M_{n,NMR}$ = 2480, 0.53 g, 0.214 mmol), and DMF (2.9 mL) were added to a glass tube under nitrogen and stirred at 60 °C for 40 h. After that, to the mixture was added 0.50 g of SiO₂-g-PDMA, and the contents were further reacted at 60 °C for 20 h. PSt star (0.367 g, 59.8% yield) was recovered by filtration, concentration, and precipitation into cold methanol. GPC-MALLS: $M_{n,MALLS}$ = 66 900, PDI = 1.18. Other multiarm stars were synthesized and isolated according to a similar approach.

PSt Star. ¹H NMR (CDCl₃): δ 7.85 (PhH), 6.2–7.6 (PhH and ArH), 5.35 (CHS), 4.67 (CH₂O of reacted DMA unit), 4.53 (CH₂S), 4.06 (CH₂O of DMA unit and CH₂OCO of PSt segment), 3.64 (OCH₂CH₂N⁺(CH₃)₂CH₂), 3.30 (OCH₂CH₂N⁺(CH₃)₂CH₂, and CH₂ of terminal DMA unit), 0.5–2.7 (CH₂N and CH₃ of DMA unit, and CH, CH₂ and CH₃ of PSt and branched core). FT-IR (KBr): 3423, 3082, 3059, 3025, 3001, 2923, 2850, 1944, 1871, 1806, 1732,

1663, 1601, 1582, 1493, 1452, 1385, 1177, 1153, 1028, 908, 842, 758, 699 $\rm cm^{-1}$

PMMA Star. ¹H NMR (CDCl₃): *δ* 7.85 (PhH), 6.2–7.8 (PhH and ArH), 5.35 (CHS), 4.58 (CH₂O of reacted DMA unit), 4.53 (CH₂S), 4.21 (CH₂O of DMA unit and CH₂OCO of PMMA segment), 3.60 (OCH₂CH₂N⁺(CH₃)₂CH₂ and CH₃O of PMMA), 3.15 (OCH₂CH₂N⁺(CH₃)₂CH₂, and CH₂ of terminal DMA unit), 0.5–2.9 (CH₂N and CH₃ of DMA unit, and CH, CH₂ and CH₃ of PMMA and branched core). FT-IR (KBr): 3448, 2998, 2951, 2851, 1730, 1484, 1450, 1389, 1274, 1243, 1196, 1148, 1061, 987, 911, 841, 750, 690 cm⁻¹.

PtBA Star. ¹H NMR (CDCl₃): δ 7.96, 7.53, and 7.37 (PhH), 4.63 (CH₂O of reacted DMA unit, CHS of PtBA and CH₂S), 4.26 and 4.19 (CH₂O of DMA unit and CH₂OCO of PtBA segment), 3.62 and 3.33 (OCH₂CH₂N⁺(CH₃)₂CH₂, and CH₂ of terminal DMA unit), 0.5–3.0 (CH₂N and CH₃ of DMA unit, and CH, CH₂ and CH₃ of PtBA and branched core). FT-IR (KBr): 3436, 3003, 2979, 2934, 2873, 1729, 1481, 1458, 1394, 1368, 1258, 1149, 1034, 909, 846, 752, 690 cm⁻¹.

PNIPAM Star. ¹H NMR (CDCl₃): δ 7.96, 7.56, and 7.40 (m, PhH), 6.0–7.2 (broad, NH of PNIPAM), 4.58 (CH₂O of reacted DMA unit and CH₂S), 4.24 (CH₂O of DMA unit and PNIPAM segment), 4.01 (CH of PNIPAM), 3.62 and 3.18 (OCH₂CH₂N⁺(CH₃)₂CH₂, and CH₂ of terminal DMA unit), 0.5–3.0 (CH₂N and CH₃ of DMA unit, and CH, CH₂ and CH₃ of PNIPAM and branched core). FT-IR (KBr): 3436, 3073, 2973, 2933, 2876, 1735, 1655, 1545, 1459, 1388, 1368, 1264, 1173, 1131, 1036, 913, 840, 691 cm⁻¹.

PCL Star. ¹H NMR (CDCl₃): δ 7.95 (PhH), 6.2–7.8 (PhH and ArH), 5.35 (CHS), 4.58 (CH₂O of reacted DMA unit and CH₂S), 4.21 (CH₂O of DMA unit, and CH₂OCO of PCL segment), 4.06 (CH₂O of PCL), 3.64 and 3.42 (OCH₂CH₂N⁺(CH₃)₂CH₂, and CH₂ of terminal DMA unit), 0.5–2.7 (CH₂N and CH₃ of DMA unit, and CH, CH₂ and CH₃ of PCL and branched core). ¹³C NMR (DMSO- d_6): δ 222.5 (C=S), 177.2, 176.7, 176.2, 172.9, 172.8 (C=O), 132.2, 124.6 (ArC and PhC), 63.5 (CH₂O of PCL and DMA unit), 60.8 $(CH_2N^+(CH_3)_2CH_2CH_2CH_2OCO), 60.6 (CH_2OH), 60.3$ (CH₂N⁺(CH₃)₂CH₂CH₂CH₂OCO), 56.5 (CH₂N of DMA unit), 53.2 (CH₂ of DMA unit), 50.6 (CH₂N⁺(CH₃)₂CH₂CH₂CH₂OCO), 45.3 (CH₃N of DMA unit), 44.3 (CH₃CCOO of DMA unit, CH₂S, CHS and CH₃CS), 33.4 (CH₂COO of PCL), 32.2 (CH₂CH₂OH), 27.9 (CH₂CH₂CH₂CH₂CO of PCL), 25.0 (CH₂CH₂CH₂CH₂CO of PCL), 24.5 (CH₂CH₂CH₂OH), 24.2 (CH₂CH₂CH₂CH₂CO of PCL), 22.4, 22.1, 21.8 (CH₂N⁺(CH₃)₂CH₂CH₂CH₂OCO), 18.6, 16.7 (CH₃)

of DMA unit). FT-IR (KBr): 3437, 2945, 2866, 1727, 1471, 1420, 1396, 1367, 1296, 1245, 1190, 1164, 1106, 1046, 962, 732 cm⁻¹.

Synthesis of $A_m B_n$ Miktoarm Stars by Successive Menschutkin Reaction. To a glass tube were added branched PVD (0.50 g, 2.67 mmol DMA unit), PCL-Br ($M_{n,NMR}$ = 1690, 0.90 g, 0.53 mmol), and DMF (7.0 mL), and the contents were reacted at 60 °C for 40 h under nitrogen. PCL star (1.36 g, 95.6% yield) was recovered by concentration and precipitation into cold hexane. GPC-MALLS: $M_{n,MALLS}$ = 23 800, PDI = 1.11.

The mixture of PCL star (100 mg, 0.155 mmol of DMA unit), PSt-Br ($M_{n,NMR}$ = 2480, 193 mg, 0.078 mmol), and DMF (1.5 mL) was stirred at 60 °C for 40 h under nitrogen and followed by addition of 0.35 g of SiO₂-*g*-PDMA and further stirring at 60 °C for 20 h. (PCL)_{*m*}(PSt)_{*n*} star (183 mg, 43.0% yield) was recovered by filtration, concentration, and precipitation into cold hexane. GPC-MALLS: $M_{n,MALLS}$ = 45 700, PDI = 1.13. Other miktoarm stars were synthesized and purified according to a similar approach.

 $(PCL)_m(PSt)_n$ Star. ^TH NMR $(CDCl_3)$: δ 7.96 and 7.85 (PhH), 6.2– 7.7 (PhH and ArH), 5.35 (CHS), 4.64 (CH₂O of reacted DMA unit and CH2S), 4.23 and 4.18 (CH2O of DMA unit, and CH2OCO of PCL and PSt segments), 4.06 (CH2O of PCL), 3.63 and 3.37 $(OCH_2CH_2N^+(CH_3)_2CH_2)$ and CH_2 of terminal DMA unit), 0.5-3.0 (CH₂N and CH₃ of DMA unit, and CH, CH₂ and CH₃ of PCL, PSt and branched core). ¹³C NMR (DMSO-d₆): δ 222.6 (C=S), 177.3, 176.9, 176.4, 176.1, 175.6, 174.4, 172.8, 171.8 (C=O), 145.2, 128.6, 128.0, 127.4, 126.6, 125.7 (ArC and PhC), 118.1 (CN), 63.5 (CH₂O of PCL and DMA unit), 61.5, 61.1, 60.8 (CH₂N⁺(CH₂)₂CH₂CH₂CH₂-OCO), 60.6 (CH₂OH), 60.2 (CH₂N⁺(CH₃)₂CH₂CH₂CH₂OCO), 55.8 (CH₂N of DMA unit), 53.5 (CH₂ of DMA unit), 50.6 $(CH_2N^+(CH_3)_2CH_2CH_2CH_2OCO)$, 45.2 $(CH_3N \text{ of DMA unit})$, 44.5 (CH₃CCOO of DMA unit, CH₂ of PSt, CH₂S, CHS and CH₃CS), 35.5, 35.2, 35.0, 34.4 (CH of PSt), 33.4 (CH₂COO of PCL), 32.3 (CH₂CH₂OH), 29.2 (CH₂COO), 27.9 (CH₂CH₂CH₂CH₂CO of PCL), 25.0 (CH₂CH₂CH₂CH₂CO of PCL), 24.5 (CH₂CH₂CH₂OH), 24.2 (CH₂CH₂CH₂CH₂CO of PCL), 22.4, 22.1, 21.8 (CH₂N⁺(CH₃)₂CH₂CH₂CH₂OCO), 18.1, 16.4 (CH₃ of DMA unit). FT-IR (KBr): 3437, 3060, 3027, 2962, 2929, 2855, 1733, 1659, 1630, 1601, 1492, 1453, 1396, 1261, 1162, 1097, 1021, 909, 864, 803, 760, 699 cm^{-1} .

(*PCL*)_m(*PMMA*)_n Star. ¹H NMR (CDCl₃): δ 6.5–8.1 (PhH and ArH), 5.35 (CHS), 4.22 (broad, CH₂O of DMA unit, CH₂S, and CH₂OCO of PCL and PMMA segments), 4.06 (CH₂O of PCL), 3.68 and 3.41 (CH₃O of PMMA, OCH₂CH₂N⁺(CH₃)₂CH₂, and CH₂ of terminal DMA unit), 0.5–3.0 (CH₂N and CH₃ of DMA unit, and CH, CH₂ and CH₃ of PCL, PMMA and branched core). FT-IR (KBr): 3438, 2995, 2951, 2868, 1732, 1658, 1628, 1484, 1452, 1390, 1365, 1276, 1245, 1190, 1148, 1062, 986, 966, 911, 843, 809, 749, 692 cm⁻¹.

 $(PCL)_m(PtBA)_n$ Star. ¹H NMR (CDCl₃): δ 6.5–8.1 (PhH and ArH), 4.24 (broad, CH₂O of DMA unit, CH₂S, and CH₂OCO of PCL and PtBA segments), 4.06 (CH₂O of PCL), 3.64 and 3.48 (OCH₂CH₂N⁺(CH₃)₂CH₂, and CH₂ of terminal DMA unit), 0.5– 3.0 (CH₂N and CH₃ of DMA unit, and CH, CH₂ and CH₃ of PCL, PtBA and branched core). FT-IR (KBr): 3438, 2978, 2936, 2865, 1730, 1629, 1478, 1461, 1393, 1369, 1258, 1151, 1037, 963, 846, 751, 690 cm⁻¹.

(*PCL*)_{*m*}(*PNIPAM*)_{*n*} Star. ¹H NMR (CDCl₃): δ 5.8−8.1 (PhH, ArH, and NH of PNIPAM), 4.1−5.0 (broad, CH₂O of DMA unit, CH of PNIPAM, CH₂S, and CH₂OCO of PCL and PNIPAM segments), 4.06 (CH₂O of PCL), 3.61 and 3.50 (OCH₂CH₂N⁺(CH₃)₂CH₂, and CH₂ of terminal DMA unit), 0.5−3.0 (CH₂N and CH₃ of DMA unit, and CH, CH₂ and CH₃ of PCL, PNIPAM and branched core). FT-IR (KBr): 3436, 3069, 2970, 2936, 2872, 2826, 2775, 1733, 1652, 1548, 1460, 1387, 1367, 1270, 1236, 1171, 1101, 1043, 966, 881, 841, 691 cm⁻¹.

Synthesis of A_mC_o Miktoarm Stars by Tandem Menschutkin Reaction and RAFT Polymerization. In a typical reaction (run 1 of Table 4), branched PVD (100 mg, 0.058 mmol CTA, 0.533 mmol DMA unit), PCL-Br (180 mg, 0.107 mmol), St (1.21 g, 11.6 mmol), and AIBN (1.9 mg, 0.012 mmol) were added to a glass tube, and dry DMF was added until the total volume was 7.7 mL. The tube with a magnetic stirring bar was sealed with a rubber septum, and the contents were degassed with bubbled nitrogen for 20 min and polymerized at 60 °C for 24 h. Monomer conversion was determined to be 22.4% by ¹H NMR analysis of polymer solution. After concentration and precipitation into cold hexane, 0.52 g of $(PCL)_m(PSt)_n$ star was obtained. GPC-MALLS: $M_{n,MALLS} = 48100$, PDI = 1.11. Other star copolymers were synthesized and purified according to a similar approach.

Characterization. The apparent number-average molecular weight $(M_{n,GPC})$ and polydispersity index (PDI) of homopolymers were measured on a Waters 150-C gel permeation chromatography using three Ultrastyragel columns (pore size 50, 100, and 1000 nm, with molecular weight ranges of 100-10 000, 500-30 000, and 5000-600 000, respectively) with 10 μ m bead size at 35 °C. THF was used as an eluent at a flow rate of 1.0 mL/min, polystyrene samples were calibrated with PSt standard samples, and other samples were calibrated using PMMA standard samples. Gel permeation chromatography with multiple angle laser scattering detection (GPC-MALLS) systems was used to determine the absolute number-average molecular weight $(M_{n,MALLS})$ of branched and star polymers, in which GPC was conducted in DMF at 40 °C with a flow rate of 1.0 mL/min, and three MZ-Gel SDplus columns (pore size 10³, 10⁴ and 10⁵ Å, with molecular weight ranges of 1000-40 000, 4000-500 000, and 10 000-2 000 000, respectively) with 10 μ m bead size were used. Detection systems consisted of a RI detector (Optilab rEX) and a multiangle $(14^{\circ}-145^{\circ})$ laser light scattering (MALLS) detector (DAWN HELLOS) with the He-Ne light wavelength at 658.0 nm. The refractive index increment dn/dc for samples were measured off-line by Optilab rEX refractive index detector (λ = 658 nm) at 25 °C using a series of different concentration solutions, and the data were collected and processed by use of ASTRA software from Wyatt Technology. ¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were recorded on a Varian spectrometer at 25 °C using CDCl₃ or DMSO- d_6 as a solvent. Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer 2000 spectrometer using KBr discs. C, H, N, and S were determined by combustion followed by chromatographic separation and thermal conductivity detection using a Carlo-Erba EA 1110CHNO-S elemental analyzer. Differential scanning calorimetry (DSC) analysis was performed under a nitrogen atmosphere using a SDT 2960 simultaneous DSC-TGA of TA Instruments, and the heating rate was 10 °C/min.

RESULTS AND DISCUSSION

This study aimed at versatile synthesis of multiarm and miktoarm stars by combination of Menschutkin reaction and RAFT process. Three types of ion-containing star polymers, namely, A_m -type multiarm stars, and $A_m B_n$ - and $A_m C_o$ -type miktoarm stars, were synthesized to confirm the great potential of these approaches, in which the branched core was generated by RAFT copolymerization of VBDB and DMA via SCVP, A and B segments were prefabricated by ring-opening polymerization (ROP) or RAFT polymerization, and C segment was directly grown from the surface of PVD via RAFT polymerization. The detailed syntheses are described below.

Synthesis of Branched PVD. Our previous study has confirmed that the target branched copolymers with variable degree of branching (DB), polydispersity index (PDI), and CTA functionality (F) could be achieved by changing feed ratios and reaction time during RAFT copolymerization of *S*-(4-vinyl)benzyl *S'*-propyltrithiocarbonate (VBPT) and vinyl monomers.⁷⁸ In this study, RAFT copolymerization of VBDB and DMA was performed to generate branched PVD with controlled number of dithiobenzoate moieties and tertiary amino groups, in which a polymerizable dithiobenzoate VBDB⁷⁵ was used instead of VBPT so as to better control RAFT process of methacrylate-type monomer.

The utilization of branched copolymers with narrow molecular weight distribution was crucial to the subsequent synthesis of well-defined star polymers. To this end, RAFT copolymerization of VBDB and DMA was performed under different conditions to generate branched PVD with relatively low polydispersity (Table 1). In ¹H NMR spectra of PVD (Figure 1), the signals of aromatic protons originating from



Figure 1. ¹H NMR spectra of PVD branched copolymers obtained by RAFT copolymerization of VBDB and DMA. The samples were synthesized by runs 1 (a), 2 (b), 3 (c), and 4 (d) of Table 1.

VBDB were noted at δ 7.98 (2H of PhH, terminal PhC(=S)S) and 6.7-7.7 (ArH and other PhH), and characteristic signals of $CH_2C(CH_3)(COOCH_2CH_2N(CH_3)_2)S$ (terminal DMA unit), CH₂S (VBDB unit with unreacted dithiobenzoate moiety) and CHS (styryl unit originated from reacted VBDB) appeared at δ 3.30 (k), 4.53 (q), and 5.0-5.5 (b); thus, proportions of dithiobenzoate functionality connecting with benzyl group (P_1) , terminal DMA unit (P_2) , and styryl unit (P_3) in branched PVD were obtained. The real repeat units per branch (RB) were deduced by equation RB = $RB(th)/(1 - P_1)$ since the proportion of remaining VBDB unit only acted as conventional vinyl monomer during copolymerization. Meanwhile, numberaverage (F_n) and weight-average (F_w) CTA functionalities per branched copolymer were determined by equations F_n = $M_{n,MALLS} \times I_{7.98} / (MW_{VBDB} \times I_{7.98} + MW_{DMA} \times I_{4.06})$, and $F_w =$ $F_{\rm n} \times PDI$, in which $M_{\rm n,MALLS}$ was number-average molecular weight of PVD determined by GPC-MALLS, and MW_{VBDB} and MW_{DMA} were molecular weights of VBDB and DMA. In Table 1, the P_1 values of various branched copolymers ranged

between 0.20 and 0.30, and their $F_n(F_w)$ values were within the range of 5.0–31.7 (6.6–154).

As expected, RAFT SCVP allowed for synthesis of branched PVD with tunable molecular parameters. The copolymerizations ($[DMA]_0$:[VBDB]_0:[AIBN]_0 = DP_0:1:0.2, $[DMA]_0 = 3.0 \text{ mol/L}$, DP_0 = 5–30, runs 1–3 of Table 1) using high concentrations of comonomers and thermal initiator were liable to generate branched copolymers with broad molecular weight distribution (PDI = 3.24–4.96) in which the copolymer fractions had M_n values in the range of 2000–2 000 000 (Figure 2a–c). As the concentrations of comonomers and AIBN were



Figure 2. GPC traces (normalized weight distribution) of PVD branched copolymers.

significantly reduced, the copolymerization could afford branched PVD with polydispersity as low as 1.32 (Figure 2d), similar to those obtained by RAFT copolymerization of VBPT and methyl acrylate in our previous study.⁷⁸ The branched PVD ($M_{n,MALLS} = 8630$, $F_n = 5.0$, with average DMA units of 46) synthesized by run 4 of Table 1 was chosen as an ideal multifunctional core for the subsequent synthesis of multiarm and miktoarm stars.

Synthesis of Bromide-Terminated Polymers. RAFTsynthesized polymers involving polystyrene (PSt-Br, $M_{n,NMR}$ = 2480, 4520, 6250, and 9600), poly(methyl methacrylate) (PMMA-Br, $M_{n,NMR}$ = 3860), poly(*tert*-butyl acrylate) (PtBA-Br, $M_{n,NMR}$ = 5050), and poly(*N*-isopropylacrylamide) (PNIPAM-Br, $M_{n,NMR}$ = 3030) were synthesized by RAFT polymerization mediated by BBCP, and bromide-terminated poly(ε -caprolactone) (PCL-Br, $M_{n,NMR}$ = 1690) was generated by ROP initiated with 3-bromo-1-propanol (Table S1).

In ¹H NMR spectra of PM-Br (Figure 3 and Figure S3), the signals of characteristic protons were observed at around δ 6.2–7.2 (PhH of PSt), 3.60 (CH₃O of PMMA), 2.23 (CH of PtBA), 1.44 (CH₃ of PtBA), 4.01 (CH of PNIPAM), 4.06 (CH₂O of PCL), 4.24 (terminal CH₂O), and 3.47 (terminal CH₂Br), and thus number-average molecular weights determined by ¹H NMR ($M_{n,NMR}$) were obtained. The apparent number-average molecular weights ($M_{n,GPC}$) of PM-Br were estimated to be 2790–9450 by GPC, and their polydispersity indices ranged from 1.06 to 1.15 (Figure 4 and Figure S4). The $M_{n,NMR}$ values were very close to those expected ($M_{n,th}$), as expected from the "living"/controlled polymerization systems.

Synthesis of A_m -Type Multiarm Stars by Menschutkin Reaction. Menschutkin reaction was normally applied for postmodification of functional polymers to generate ion-bearing segments.^{79,81–86} In this study, bromide-terminated



Figure 3. ¹H NMR spectra of bromide-functionalized polymers.



Figure 4. GPC traces of PM-Br (PM = PSt (a), PMMA (b), PtBA (c), PNIPAM (d), and PCL (e)).

polymers were directly coupled onto the surface of branched PVD via quaternization process, allowing for the straightforward synthesis of multiarm and miktoarm stars with lowered reaction steps.

Many factors such as reaction temperature, concentration, time, feed ratio, chain rigidity, and molecular weight can affect Menschutkin reaction between branched copolymer bearing DMA units and bromide-terminated polymers. The reactions between PVD and PM-Br using a fixed polymer concentration of 0.20 g/mL were conducted in DMF at 60 $^{\circ}$ C, and syntheses

of PSt stars were taken as typical examples to investigate the influence of reaction conditions. After coupling reaction, PDMA grafted silica particles (SiO₂-g-PDMA) were added to the reaction system to perform a subsequent Menschutkin reaction, and the remaining unreacted PM-Br was grafted onto the surface of solid substrates to form comblike copolymer grafted silica via quaternization process. The resultant star polymers with a branched core could be efficiently isolated via filtration and precipitation owing to the poor solubility of silica-copolymer hybrids in organic solvents. This method could completely remove unreacted PM-Br, evident from GPC-MALLS and NMR spectra as described later, in which GPC traces of the isolated stars only exhibited monomodal distribution, and characteristic signals corresponding to CH₂CH₂CH₂Br of PM-Br were absent in ¹H and ¹³C NMR spectra.

In ¹H NMR spectrum of PSt star (Figure 5a), the signals of characteristic protons were noted at around δ 6.2–7.6 (PhH of



Figure 5. ¹H NMR spectra of A_m -type multiarm stars with a branched core.

PSt arm, PhH and ArH of PVD core), 4.06 (CH₂O of DMA unit), 3.64 (OCH₂CH₂N⁺(CH₃)₂CH₂), and 3.30 (OCH₂CH₂N⁺(CH₃)₂CH₂, and CH₂ of terminal DMA unit). By comparing the integrated peak areas of protons at δ 6.2–7.6 and 4.06, the $M_{n,NMR}$ values of PSt stars were obtained. Meanwhile, their absolute M_n values and polydispersity indices were determined by GPC-MALLS. On this basis, average arm number (*m*) of PSt star and coupling efficiency (CE) of Menschutkin reaction were calculated by equations $m = (M_{n,star})$

 $-M_{n,PVD})/M_{n,arm}$, and CE = $m/46r_0$, in which $M_{n,star}$ and $M_{n,PVD}$ were number-average molecular weights of PSt star and PVD determined by GPC-MALLS, $M_{n,arm}$ was $M_{n,NMR}$ value of PSt-Br, 46 meant average number of DMA units per PVD, and r_0 was feed ratio of PSt-Br to DMA unit of PVD.

First, the reactions $(M_{n,NMR}(PSt-Br) = 2480, r_0 = 0.80)$ were performed in DMF at 60 °C for different time to reveal the effects of reaction time on coupling reaction (runs 1-4 of Table 2 and Figure S6). No significant enhancement in $M_{\rm n,MALLS}$ was noted as the time was beyond 40 h, originating from the enhanced shielding effect with increasing grafting density. When the arm number of the resultant stars was high enough, the surface of branched PVD was almost surrounded by the grafted PSt chains, and thus PSt-Br segments were quite difficult to approach DMA units to further perform the quaternization process. As the reaction time increased from 3.5 to 40 h, the *m* value of multiarm stars was significantly increased from 9.1 to 23.5, and the coupling efficiency was enhanced from 24.6% to 63.8%. Their PDI values were around 1.2, and no obvious shoulder and tailing were noted in GPC traces, revealing the absence of notable side reactions during star formation. Consequently, 40 h was chosen as the suitable time for quaternization reaction between PVD and PM-Br.

Second, the reactions of branched PVD and PSt-Br with different molecular weights were conducted to investigate the effects of arm length on coupling reaction (runs 4–7 of Table 2). The resultant PSt stars were of $M_{n,MALLS}$ values in the range of 63 800–76 900, with polydispersity indices lower than 1.22. As $M_{n,NMR}$ values of PSt segments increased from 2480 to 9600, the arm number of star polymers obtained significantly decreased from 23.5 to 7.1, and the CE values were correspondingly reduced from 63.8% to 19.3% (Figure S7), which could be ascribed to lowered quaternization reactivity and enhanced steric hindrance with increasing molecular weight of grafted chains. These results indicated that Menschutkin reaction between PVD and PSt-Br could be efficiently performed as the grafted PSt chains were relatively short.

Last, quaternization reactions in a wide range of r_0 ($W_{polymer}$: $V_{DMF} = 0.20$ g/mL, $M_{n,NMR}$ (PSt-Br) = 4520) were carried out to reveal the influence of feed ratio on coupling reaction (runs 5 and 8–10 of Table 2). As r_0 increased from 0.20 to 1.0, the $M_{n,MALLS}$ values of PSt stars increased from 40 100 to 66 400, and their polydispersity indices were in the range of 1.16 and 1.24. With increasing amount of PM-Br, the coupling efficiency was significantly decreased from 75.7% to 27.8% although the arm number gradually increased from 7.0 to 12.8 (Figure S8). Consequently, multiarm PSt stars with higher arm number could be achieved at the cost of using sacrificial PSt-Br.

On this basis, other PMMA, PtBA, PNIPAM, and PCL stars were synthesized (runs 11–15 of Table 2). In ¹H NMR spectra of isolated stars (Figure 5b–e), the signals of characteristic protons of each arm and branched core were noted at about δ 3.60 (CH₃O of PMMA), 2.23 (CH of PtBA), 4.01 (CH of PNIPAM), 4.06 (CH₂O of PCL and DMA unit), 7.8–8.1 (terminal PhH of PhC(=S)S moieties), and 3.2–3.8 (OCH₂CH₂N⁺(CH₃)₂CH₂). By comparing the integrated peak areas of these protons, $M_{n,NMR}$ values of various stars were obtained. The $M_{n,MALLS}$ and $M_{n,NMR}$ values were usually similar, and both were in good accordance with $M_{n,th}$ results expected from $M_{n,MALLS}$ (PVD), $M_{n,NMR}$ (PM-Br), and yield of isolated stars. The number of arms was in the range of 9.0– 35.1, with coupling efficiency ranging from 39.0% to 97.6%. Various stars were liable to exhibit symmetric distribution in GPC traces, with polydispersity indices in the range of 1.10–1.24 (Figure 6), suggesting the coupling reaction was efficiently performed.



Figure 6. GPC traces (normalized weight distribution) of multiarm stars with a branched core. $M_{n,MALLS}$ and PDI of various stars were 76 900, 1.11 (PSt star), 66 800, 1.10 (PMMA star), 81 100, 1.13 (PtBA star), and 76 500, 1.24 (PNIPAM star).

The above results revealed that the Menschutkin reaction between polymers was strongly dependent on reaction conditions, and A_m -type multiarm stars with arm number up to 35.1 could be achieved under optimized conditions, in which the coupling efficiency was normally in the range of 19.3– 97.6%. The versatile and general reaction allowed for efficient synthesis of a variety of well-defined multiarm stars by control over reaction time and feed ratio of PM-Br to PVD.

Synthesis of $A_m B_n$ -Type Miktoarm Stars by Successive Menschutkin Reactions. Multistep Menschutkin reactions are potentially applicable for the synthesis of many types of miktoarm stars such as $A_m B_n$, $A_m B_n C_o$, and even $A_m B_n C_o D_p$ stars. As the chain lengths of various arms are relatively short, the approach to synthesis of miktoarm stars via successive coupling reactions is very promising due to its high coupling efficiency.

To confirm the great potential of such methodology in construction of miktoarm stars, A_m -type PCL star ($M_{n,MALLS}$ = 23 800, $m \approx 9.0$, with average DMA units of 37) synthesized by run 14 of Table 2 was used to synthesize $A_m B_n$ stars by a second Menschutkin reaction. The reactions using feed ratio of PM-Br to DMA unit of PCL star (r_0) in the range of 0.30-0.80 afforded $A_m B_n$ (A = PCL; B = PSt, PMMA, PtBA, and PNIPAM) miktoarm stars (Table 3). In ¹H NMR spectra of isolated stars (Figure 7), the signals of characteristic protons of each arm and branched core appeared at about δ 6.2–7.2 (PhH of PSt), 3.60 (CH₃O of PMMA), 2.23 (CH of PtBA), 1.44 (CH3 of PtBA), 6.0-7.2 (NH of PNIPAM), 4.01 (CH of PNIPAM), 4.06 (CH₂O of PCL and DMA unit of branched core), 7.8–8.1 (terminal PhH of PhC(=S)S moieties), and 3.2-3.8 (OCH₂CH₂N⁺(CH₃)₂CH₂). The $M_{n,MALLS}$ and $M_{n,NMR}$ values of various stars were similar, and both were close to $M_{\rm n.th}$ values expected from $M_{n,MALLS}$ (PCL star), $M_{n,NMR}$ (PM-Br), and yield of isolated stars. GPC-MALLS results revealed Menschutkin reaction between PCL star and PM-Br could afford $A_m B_n$ stars with $M_{n,MALLS}$ values ranging from 42 200 to 67 500, and the arm number of B segment was calculated to be in the range of 6.1–11.3. These results indicated that the target $A_m B_n$ stars with tunable arm number of B segment could be efficiently

Table 3. Results for Synthesis of $A_m B_n$ (A = PCL, B = PM, $m \approx 9.0$) Miktoarm Stars by Menschutkin Reaction between PCL Star and PM-Br^{*a*}

run	PM	r_0^b	Y (%) ^c	$M_{ m n,th}^{d}$	$M_{\rm n,MALLS}^{e}$	PDI ^e	$M_{\rm n,NMR}^{f}$	n ^g	CE $(\%)^h$
1	PSt	0.50	43.0	43 500	45 700	1.13	44 100	8.8	47.6
2	PMMA	0.80	39.5	68 900	67 500	1.16	66 900	11.3	38.2
3	PtBA	0.50	34.8	56 300	58 100	1.20	55 800	6.8	36.8
4	PNIPAM	0.30	50.6	40 800	42 200	1.09	41 600	6.1	55.0

^{*a*}Reaction conditions: $M_{n,NMR} = 2480$ (PSt-Br), 3860 (PMMA-Br), 5050 (PtBA-Br), 3030 (PNIPAM-Br); $W_{polymer}$: $V_{DMF} = 0.20$ g/mL, in DMF at 60 °C for 40 h. ^{*b*}Molar ratio of PM-Br to DMA unit of PCL star. 'Yield of isolated star copolymer. ^{*d*}Theoretical molecular weight. ^{*c*}Number-average molecular weight and polydispersity determined by GPC-MALLS. ^{*f*}Number-average molecular weight determined by ¹H NMR. ^{*g*}Average arm number of PM segment in star copolymer, $n = (M_{n,AmBn} - M_{n,Am})/M_{n,PM}$, in which $M_{n,AmBn}$ and $M_{n,Am}$ were molecular weights of A_mB_n and PCL stars determined by GPC-MALLS, ^{*f*}Coupling efficiency of Menschutkin reaction, CE = $n/37r_0$, in which 37 was average number of DMA unit per PCL star.



Figure 7. ¹H NMR spectra of $A_m B_n$ stars with a branched core (A = PCL; B = PSt (a), PMMA (b), PtBA (c), and PNIPAM (d)).

synthesized via two-step Menschutkin reactions, in which A and B arms could be any polymer segments soluble in DMF.

With increasing grafting density of arm segments, the successive syntheses of miktoarm stars may suffer from some disadvantages involving enhanced steric hindrance and heterogeneity, resulting in lowered coupling efficiency, broadened molecular weight distribution, and different chemical composition among miktoarm stars. As compared with their precursors PVD and PCL star, the GPC traces of the resultant $A_m B_n$ stars exhibited monomodal distribution and completely shifted to higher molecular weight sides (Figure 8), corresponding to the efficient quaternization process. The polydispersity indices of $A_m B_n$ stars determined by GPC-MALLS were lower than 1.20, and the coupling efficiency was



Figure 8. GPC traces (normalized weight distribution) of branched PVD (a), PCL star (b), and $(PCL)_m(PM)_n$ miktoarm stars (PM = PSt (c), PMMA (d), PtBA (e), and PNIPAM (f)).

within the range 36.8–55.0%, suggesting the above-mentioned limitations were not obvious.

In addition to ¹H NMR and GPC-MALLS, ¹³C NMR spectroscopy was also used to characterize representative polymer samples. In ¹³C NMR spectrum of branched PVD (Figure 9a), characteristic signals of aromatic carbons and DMA units appeared at δ 175.8–176.8 (C=O), 126.7–145.0 (ArC and PhC), 62.4 (CH₂O), 56.6 (CH₂N), 45.1 (CH₃N), and 44.2 (CH₂CCOO). For PCL star with a branched core (Figure 9b), characteristic signals corresponding to PCL arms were noted at δ 172.8 (C=O), 63.5 (CH₂O), 60.6 (CH₂OH), 33.4 (CH₂COO), 32.2 (CH₂CH₂OH), 27.9 (CH₂CH₂- $CH_2CH_2CO)$, 25.0 ($CH_2CH_2CH_2CO$), 24.5 (CH₂CH₂CH₂OH), and 24.2 (CH₂CH₂CH₂CH₂CO), and typical signals beside the ionic bonds appeared at δ 60.8 (CH₂N⁺(CH₃)₂CH₂CH₂CH₂OCO), 60.3 (CH₂N⁺(CH₃)₂CH₂-CH₂CH₂OCO), 50.6 (CH₂N⁺(CH₃)₂CH₂CH₂CH₂OCO), and 22.4 (CH₂N⁺(CH₃)₂CH₂CH₂CH₂OCO). In the ¹³C NMR spectrum of $(PCL)_m(PSt)_n$ star (Figure 9c), characteristic signals of PSt and PCL segments appeared at δ 145.2, 125.7– 128.6 (PhC), 44.5 (CH₂ of PSt), 63.5, 33.4, 27.9, 25.0, and 24.2 $(CH_2 \text{ of PCL})$, and typical signals corresponding to $CH_2N^+(CH_3)_2CH_2CH_2CH_2OCO$ were observed at δ 61.5, 61.1, 60.8, 60.2, 50.6, and 22.4. The signals of unbonded DMA units at δ 56.6 (CH₂N) and 45.1 (CH₃N) were significantly weakened, and new signals corresponding to CH₂N⁺(CH₃)₂CH₂CH₂CH₂OCO were noted in ¹³C NMR spectra, confirming the success of Menschutkin reaction between branched PVD and PM-Br. The isolated multiarm stars lacked signals at 62.1, 31.3, and 31.0 (BrCH₂CH₂CH₂O of



Figure 9. ¹³C NMR spectra of branched PVD (a), PCL star (b), and $(PCL)_m(PSt)_n$ star (c) in DMSO- d_6 .

PSt-Br) and 61.8, 31.3, and 30.9 (BrCH₂CH₂CH₂O of PCL-Br) in ¹³C NMR spectra and only exhibited monomodal distribution in GPC traces, revealing the absence of PM-Br. These results further demonstrated Menschutkin reaction between polymers could be efficiently applied for the synthesis of multiarm and miktoarm stars with low polydispersity.

Synthesis of A_mC_o -Type Multiarm Stars by Tandem Menschutkin Reaction and RAFT Polymerization. Suc-

cessive coupling reactions are very efficient to synthesize miktoarm stars with relatively short arms; however, the coupling efficiency is gradually decreased with increasing grafting density, and thus it is difficult to synthesize $A_m B_n$ miktoarm stars with same arm number and different arm length of B segment. The tandem reaction is promising to partly address this disadvantage. The alternative method allows for facile construction of $A_m C_o$ stars via simultaneous Menschutkin reaction and RAFT polymerization, in which A segment can be efficiently grafted onto the surface of PVD via quaternization process, the arm length of RAFT generated C segment can be adjusted by control over reaction time and feed ratio, and the arm number of C segment is equal to the CTA functionality of branched core as the dithiobenzoate moieties are quantitatively activated.⁷⁸

The simultaneous coupling reaction between PCL-Br $(M_{n,NMR} = 1690)$ and PVD $(M_{n,MALLS} = 8630)$ and RAFT polymerization of St, tBA, and NIPAM mediated by PVD were performed in DMF at 60 °C for 24 h (Table 4). In ¹H NMR spectrum of branched PVD (Figure 1), the signals of characteristic protons connecting with terminal CTA functionalities were noted at δ 5.0–5.5 (CHS), 4.53 (CH₂S), and 3.30 (CH₂ of terminal DMA unit). These signals completely disappeared in ¹H NMR spectra of isolated A_mC_o stars (Figure 10), and a new signal corresponding to CHS of terminal monomer unit was quantitatively observed at δ 4.6–4.9, confirming the RAFT polymerization to grow C segment was efficiently conducted. Other characteristic signals appeared at δ 4.06 (CH₂O of PCL), 6.2-7.2 (PhH of PSt), 2.23 (CH of PtBA), 1.44 (CH₃ of PtBA), 6.0-7.0 (NH of PNIPAM), 4.01 (CH of PNIPAM), 1.13 (CH₃ of PNIPAM), and about 7.96 (2H of PhH, terminal PhC(=S)S). By comparing the integrated peak areas of dithiobenzoate moiety, CH2O of PCL and characteristic protons of other C segment, the total number of monomer units per star could be deduced. The average arm number of PCL in $A_m C_a$ stars was estimated to be in the range of 8.8–9.0 by ¹H NMR analysis, corresponding to coupling efficiency of 96-98%. By assuming the arm number of C segment was equal to the CTA functionality of PVD (F_n = 5.0), the polymerization degree of each arm was determined to be 43.2 (PSt), 49.5 (PtBA), and 43.6 (PNIPAM) by ¹H NMR. The $M_{n,NMR}$ and $M_{n,MALLS}$ values of A_mC_o stars were comparable, and both were close to the $M_{n,th}$ values expected from $M_{n,MALLS}$ (PVD), monomer conversion (C%), and the assumed quantitative coupling efficiency. The GPC traces of various stars exhibited monomodal distribution and wholly shifted to higher molecular weight side than PVD, with PDI values lower than 1.12 (Figure 11), revealing the successful synthesis of the target miktoarm stars via the tandem approach.

The above results revealed the tandem reaction could afford A_mC_o stars ($m \approx 8.8-9.0$, $o \approx 5.0$) with well-controlled molecular weight and low polydispersity. It should be mentioned that a subsequent Menschutkin reaction or fractional precipitation may be necessary to remove the unreacted bromide-functionalized A segment if its chain length is too long to efficiently perform the quaternization reaction. This approach is promising for the synthesis of miktoarm stars with tunable arm number of short A segment and variable chain length of C segment since it combines the advantages of "grafting onto" and "core first" approaches.²¹⁻²⁷ Owing to the nature of "living"/controlled polymerization of RAFT process, A_mC_o star copolymers with molecular weight of C segment up

Article

Table 4. Results for Synthe	sis of $A_m C_o$ (A = PCL)	$C = PM, o \approx 5.0$) Miktoarm Stars by	Tandem Menschutk	in Reaction and
RAFT Polymerization ^a					

run	М	$[M]_0 (mol/L)$	C (%) ^b	$M_{ m n,th}{}^c$	$M_{n,MALLS}^{d}$	PDI^d	$M_{ m n,NMR}^{e}$	m^{f}
1	St	1.5	22.4	47 500	48 100	1.11	46 000	8.8
2	tBA	1.0	48.8	55 400	53 600	1.06	55 200	8.8
3	NIPAM	1.0	44.5	49 300	50 000	1.12	48 500	9.0





Figure 10. ¹H NMR spectra of $A_m C_o$ stars with a branched core.

to tens of thousands are potentially achieved by the tandem approach under optimized conditions.

DSC Analysis and Solubility of Multiarm and Miktoarm Stars. To investigate the effects of macromolecular architecture on chain relaxation and melting behaviors, glass transition (T_g) and melting (T_m) temperatures of various stars and their precursors were determined by DSC (Table S2). Branched PVD ($M_{n,MALLS} = 8630$) had a glass transition at 28.6 °C, and bromide-terminated polymers possessed a glass transition at 66.0 (PSt-Br, $M_{n,NMR}$ (PSt-Br) = 2480), 77.4 (PMMA-Br), 31.3 (PtBA-Br), and 107.6 °C (PNIPAM-Br). PCL-Br was of two melting peaks at 43.3 and 46.6 °C (Figure 12a), while PCL star had a decreased T_m at 35.4 °C (Figure 12b). As compared with PM-Br, the resultant (PM)_m-type multiarm stars except PCL star exhibited one enhanced T_g in the range of 36.5–125.3 °C (Figure 12b), in which the



Figure 11. GPC traces (normalized weight distribution) of branched PVD (a) and A_mC_o -type miktoarm stars (A = PCL; C = PSt (b), PtBA (c), and PNIPAM (d)).

increased value in T_g was 11.6 (PM = PSt), 15.7 (PM = PMMA), 5.2 (PM = PtBA), and 17.7 °C (PM = PNIPAM). Although the T_g values of multiarm stars were higher than their arm precursors, they were usually lower than linear PM segments with similar molecular weight. For instance, the T_g value of PSt ($M_{n,NMR} = 65\,300, T_g = 77.6$ °C) and PMMA ($M_{n,NMR} = 66\,200, T_g = 93.1$ °C) stars was lower than that of their linear chains with comparable M_n values ($T_g \approx 100$ °C). This phenomenon could be primarily attributed to the branching effect although all the factors involving arm number, segment rigidity and polarity, and chain length played important roles in chain relaxation.

On the contrary, the chain relaxation and melting behaviors of miktoarm stars were more complex. For all the miktoarm stars bearing PCL arms, the presence of noncrystalline segments strongly prevented the PCL chains from folding and rearrangement, evident from the absence of melting peak in DSC curves of $A_m B_n$ stars (Figure 12c). Meanwhile, PCL chains were liable to act as "plasticizers" during glass transition of star copolymers, resulting in remarkably decreased $T_{\rm g}$ values. No notable T_g appeared in DSC curve of $(PCL)_m(PSt)_n$ star, and the glass transition temperature of $(PCL)_m(PM)_n$ stars as noted at 71.2 (PM = PMMA), 24.9 (PM = PtBA), and 87.0 °C (PM = PNIPAM) was distinctly lower than that of PM-Br. These results indicated the presence of PCL arms tended to weaken the interactions among polymer segments, and thus the chain relaxation of PM segments in miktoarm stars could smoothly perform at significantly reduced temperatures.

In addition, multiarm and miktoarm stars with quaternary ammonium bromides usually had solubility different from those without quaternization interaction, and nine solvents comprising deionized water and hexane were used to check their solubility (Table 5). Branched PVD was insoluble in hexane



Figure 12. DSC curves of PVD and PM-Br (a), PM stars (b), and $A_m B_n$ stars (c).

and diethyl ether, partly soluble in water and DCM, and soluble in other solvents. All the multiarm and miktoarm stars were soluble in DMF, soluble or partly soluble in DCM and THF, and insoluble in hexane and diethyl ether (except PtBA star). Interestingly, all the stars except $(PCL)_m(PtBA)_n$ star were insoluble in water, and star polymers except PSt, PNIPAM, and $(PSt)_m(PNIPAM)_n$ stars were at least partly soluble in methanol. The special solubility in different solvents revealed the presence of quaternary ammonium bromides was liable to remarkably change the solubility parameter of various stars, which was mainly dependent on chain length, chemical composition, segment rigidity, and degree of ionization of DMA units. Consequently, these ion-bearing star polymers potentially exhibit unique self-assembly behaviors in water and cosolvents, which are in progress in our laboratory.

CONCLUSION

Menschutkin reaction and controlled polymerization were efficiently combined to generate Am-, AmBn-, and AmCo-type star polymers with a branched core and PCL, PSt, PMMA, PtBA, and PNIPAM arms. The Menschutkin reaction between branched PVD and PM-Br was strongly dependent on reaction conditions, and the coupling efficiency was in the range 19.3-97.6%. A series of multiarm and miktoarm stars with roughly controlled arm number and tunable chain length were achieved by control over reaction conditions and utilization of different methods, confirming the generality and versatility of these synthetic approaches. DSC results indicated the T_{σ} values decreased in the order PM star > PM-Br > $(PCL)_m(PM)_n$ star (PM = PMMA, PtBA, and PNIPAM), revealing the strong dependence of chain relaxation on macromolecular architecture. In addition, the resultant star polymers exhibited solubility different from conventional stars without ionic bonds. The ionbearing stars may have a potential utility in supramolecular chemistry and smart biomaterials due to their special thermal and solution properties.

ASSOCIATED CONTENT

Supporting Information

¹H NMR spectra of BBCP and PSt-Br, ¹³C NMR spectra of PCL-Br, PSt-Br, and branched PVD, GPC traces of PSt-Br, IR spectra of BBCP, PVD, PM-Br, and star polymers, and TGA curves of Si-TBPT and SiO₂-g-PDMA. This material is available free of charge via the Internet at http://pubs.acs.org.

sample	methanol	acetone	water	toluene	hexane	diethyl ether	DCM	THF	DMF
PVD	+	+	±	+	_	-	±	+	+
PSt star	-	-	-	±	-	-	±	+	+
PMMA star	±	±	-	±	-	-	+	+	+
PCL star	±	±	-	±	_	-	±	±	+
PtBA star	+	+	-	+	±	+	+	+	+
PNIPAM star	-	-	-	_	_	-	±	±	+
$(PCL)_m (PSt)_n$	±	+	-	+	_	-	+	+	+
$(PCL)_m(PMMA)_n$	+	+	-	+	_	-	+	+	+
$(PCL)_m (PtBA)_n$	+	+	±	+	_	-	+	+	+
$(PCL)_m(PNIPAM)_n$	-	-	-	_	_	-	±	±	+

Table 5. Solubility of PVD and Star Polymers in Various Solvents^a

^aSolubility: + (soluble), \pm (partly soluble, with solubility lower than 0.2 mg/mL), and - (insoluble).

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Grants 20874067, 21074081, and 21274096), the Key Project of Chinese Ministry of Education (No. 209049), and the Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

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