

Self-Assembly Behavior of Amphiphilic Linear-Block-Dendritic Copolymers with Long Subchains: Dependences on Dendron Generation and Mixing Dynamics

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ABSTRACT: Block copolymers composed of acrylic acid and methyl methacrylate with three topologies of double linear blocks, poly(acrylic acid) (PAA) linear block/poly(methyl methacrylate) (PMMA) G1-dendron and PAA linear block/PMMA G2dendron have been prepared by the combination of atom transfer radical polymerization and azide–alkyne click reaction. Proton nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy, and gel permeation chromatography have been adopted thoroughly to identify the chemical structure of those block copolymers with expected topologies. The self-assembly of those block copolymers in the selective solvent has been performed through two mixing routes of gentle and abrupt variation in solvent selectivity, and the morphology of the obtained self-assemblies/aggregates was observed by transmission electron microscopy. Because

INTRODUCTION Self-assembly of amphiphilic copolymers in the selective solvent has prevailed in the past decades. The studied topologies of amphiphilic copolymer can be linear diblock,¹ linear triblock,^{2,3} and miktoarm star-block,⁴ further extending to linear-*b*-dendron,⁵⁻¹² linear-*b*-hyperbranched,¹³ hyperbranched, *g*-multi-arm,^{14,15} hyperbranched-*b*-linear-*b*-hyperbranched,¹⁶ and hyperbranched-*b*-hyperbranched.¹⁷ Among them, linear-*b*dendron copolymers are more attractive due to their combination of the loose chain conformation from linear block and the compact chain conformation from dendritic segment, leading to more complicated phase-separation behavior both in bulk and solution. The synthesis of linear-b-dendron copolymer can be mainly divided to the following: the coupling strategy, the linearfirst strategy, and the dendron-first strategy.¹⁸ As for their functionality, linear-b-dendron copolymers have been exploited in the areas of drug release,¹⁹ gene delivery,²⁰ semiinterpenetrating network materials,²¹ biomineralization,²²

the abrupt variation route altered sharply the solvent quality during the mixing, the intermolecular association of polymer chains resulted in the smaller self-assemblies but the further growth of smaller self-assemblies was not observed. On the contrary, the gentle variation route changed gradually the solvent quality during the mixing, favoring not only the intermolecular association but also the further growth of selfassemblies to result in larger aggregates. The final morphology of those assemblies/aggregates also exhibited the dependence of PMMA dendron generation. © 2018 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2018**, *00*, 000–000

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special surface adsorption,¹⁰ regio-selective modification,¹⁰ stimuli-responsive device,^{23,24} photoluminescence,²⁵ and electro-chemistry.²⁶ However, the dependence of linear-*b*-dendron self-assembly on the dendron generation is still in the way of investigation.

The self-assembly behavior of linear block copolymers in the selective solvent has been well recognized. Generally, the morphology is affected by the parameters of block lengths, block length ratio, solvent selectivity, and polymer concentration. The dynamics of mixing polymer solution with selective solvent is also an important factor to control the self-assembly morphology. For example, Nose and coworkers disclosed the strong dependence of poly(*N*,*N*-dimethylacryla-mide)-*g*-poly(methyl methacryl-ate) self-assembled structure on the rate of mixing polymer/methanol solution with water.²⁷ Fast mixing induced the small self-assemblies with

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SCHEME 1 Schematic self-assembly morphologies of L-PAA-*b*-L-PMMA, L-PAA-*b*-G1-PMMA, and L-PAA-*b*-G2-PMMA via two mixing routes. [Color figure can be viewed at wileyonlinelibrary.com]

unimodal size distribution, while slower mixing rate yielded the larger self-assemblies with bimodal size distribution. Han and coworkers prepared the self-assemblies of poly(acrylic acid)-g-poly(ethylene oxide)-g-dodecyl (PAA-g-PEO-g-dodecyl) through two mixing dynamics of gentle and abrupt variation in solvent selectivity.²⁸ It was found that at low pH value and high dodecyl content, abrupt variation promoted intrachain association. Especially, Gillies and coworkers synthesized linear-*b*-dendron copolymers composed of linear poly(γ -benzyl-L-glutamate) and hydroxyl-capped polyester dendron (PBLGxb-G_v-OH, x and y indicates the chain length and the generation number, respectively).²⁹ They found that fast injection of PBLG₂₈-b-G₃-OH/DMF or PBLG₅₄-b-G₃-OH/DMF solution into water mainly induced the formation of solid aggregates, whereas slow injection of water into the polymer solution promoted the formation of assemblies like micelles and larger spherical objects.

Although the self-assembly of amphiphilic copolymers composed of linear block and short-subchain dendron has been studied, $^{5-9,29,30}$ those concerning with linear block/long-subchain dendron architecture are still rarely reported. Fan et al. synthesized linear poly(D- or L-lactide)-*block*-long-subchain dendritic PAA and studied the self-assembly properties.¹² However, as for any kind of linear-*b*-dendron copolymers, the influence of dendron generation was still not concerned.

In this work, we obtained amphiphilic PAA/poly(methyl methacrylate) (PMMA) block copolymers with three topologies such as double linear blocks, PAA linear block/ long-subchain PMMA G1-dendron, and PAA linear block/ long-subchain PMMA G2-dendron, namely, L-PAA-*b*-L-PMMA, L-PAA-*b*-G1-PMMA, and L-PAA-*b*-G2-PMMA. Their self-assemblies were prepared by two mixing dynamics: gentle and abrupt variation in solvent selectivity. As illustrated in Scheme 1, the effects of mixing dynamics and dendron generation on the self-assembly morphology have been studied in detail.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) and tert-butyl acrylate (tBA) (Sinopharm Chemical) were distilled under vacuum to remove the inhibitor. Tetrahydrofuran (THF) was refluxed over CaH₂ for 6 h, over sodium/benzophenone until it turned black-purple, then distilled for use. N,N-Dimethylformamide (DMF) was dried with anhydrous MgSO₄ and distilled under reduced pressure. Copper bromide (Sinopharm Chemical) was reduced by 0.01 M Na₂SO₃ aqueous solution, filtered, and subsequently washed with 1 wt % HBr aqueous solution, acetic acid, and alcohol for twice, sequentially. Ethyl 2-bromoisobutyrate (EBiB)³¹ and propargyl 2,2-bis((2'-bromo-2'-methyl-propanoyloxy)methyl)propionate (PBMP, NMR spectrum in Supporting Information Fig. S2)³² were prepared according to the literature. 2-Bromoisobutyryl bromide and N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA) (Sigma-Aldrich) and other chemical reagents (Aladdin) were used without further purification. Deionized water was used in the preparation of self-assemblies.

Synthesis of Propargyl 2-Bromoisobutyrate

A 250-mL round-bottomed flask was charged with propiolic alcohol (5.61 g, 100 mmol) and CH_2Cl_2 (100 mL). Then, triethylamine (11.14 g, 110.1 mmol) was added. After the mixture was kept in an ice bath for 30 min, 2-bromoisobutyryl bromide (25.29 g, 110 mmol) in CH_2Cl_2 (50 mL) was added dropwise and the reaction was left at ambient temperature overnight. The reaction mixture was washed with water (4 \times 100 mL) and the combined organic phase was dried with anhydrous Na₂SO₄. Finally, CH_2Cl_2 was removed by rotary evaporation, and the product (yield: 14.36 g, 70%) was obtained by vacuum distillation. Its NMR spectrum was shown in Supporting Information Figure S1.

Synthesis of Block Copolymers with Different Topologies Synthesis of Linear Poly(tert-butyl acrylate) Through ATRP A 100-mL round-bottomed flask was charged with EBiB (441.1 mg, 2.3 mmol), tBA (31.5 g, 245.8 mmol), PMDETA (395.5 mg, 2.3 mmol), and acetone (24 mL). After three freeze-pump-thaw cycles, CuBr (333.1 mg, 2.3 mmol) was added. The flask was kept in an oil bath controlled at 60 °C and the reaction was allowed to last for 10 h. After the reaction was quenched in liquid nitrogen, the reaction mixture was diluted with THF and passed through the neutral alumina column to remove the copper salt. After concentrated, the mixture was precipitated in methanol/water (50/50; v/v) for three times. After decantation, the polymer was dried under vacuum at ambient temperature for 24 h and obtained as a solid.

Yield: 8.26 g, $M_{n,GPC} = 4600$, PDI = 1.12. FTIR: ν (-C(CH₃)₃): 1369 cm⁻¹; ν (-C=0): 1728 cm⁻¹. ¹H NMR (CDCl₃) δ : -CH₂-O-C=0, -CH₂-CH-Br (4.01); -CH₂-CH-C=0 (2.15); -CH₂-CH-C=0, -O-C(CH₃)₃ (1.95-1.22); CH₃-CH₂-O-C=0 (1.19); O=C-C- (CH₃)₂ (1.06).

Synthesis of Linear PAA-Block-PMMA (L-PAA-b-L-PMMA)

A 100-mL round-bottomed flask was charged with linear poly(tert-butyl acrylate) (L-PtBA-Br) (5.26 g, 1.1 mmol), NaN₃ (936.7 mg, 14.4 mmol), and DMF (50 mL), and then it was kept in an oil bath at 40 °C. The reaction proceeded for 36 h. The reaction mixture was diluted with THF and passed through a neutral alumina column to remove NaN₃. Afterward, the solution was concentrated by rotary evaporation and subsequent vacuum distillation. The product L-PtBA-N₃ was obtained by thrice precipitation in methanol/water (50/ 50; v/v) and dried under vacuum at room temperature.

Yield: 4.74 g. FTIR: $v(-C(CH_3)_3)$: 1369 cm⁻¹; v(-C=0): 1728 cm⁻¹; $v(-N_3)$: 2114 cm⁻¹.

To a 25-mL Schlenk flask, L-PtBA-N₃ (1.43 g, 0.3 mmol), propargyl 2-bromoisobutyrate (PBiB) (0.1235 g, 0.6 mmol), PMDETA (52.0 mg, 0.3 mmol), and DMF (15 mL) were added, followed by the addition of CuBr (43.2 mg, 0.3 mmol) after three freeze-pump-thaw cycles. After sealed under vacuum, the Schlenk flask was kept in an oil bath preheated at 40 °C. The reaction proceeded for 12 h and quenched in liquid nitrogen. After dilution with THF, the reaction mixture was passed through neutral alumina column. Subsequently, the mixture was concentrated, precipitated in methanol/ water (50/50; v/v) for three times, and dried under vacuum at ambient temperature to obtain L-PtBA-PBiB as white powder (yield: 1.12 g).

L-PtBA-PBiB (1.003 g, 0.21 mmol), MMA (7.511 g, 75.0 mmol), PMDETA (42.5 mg, 0.25 mmol), and THF (1.25 mL) were added into a 25-mL Schlenk flask. After three freeze-pump-thaw cycles, CuBr (30.5 mg, 0.21 mmol) was added. Then the Schlenk flask was sealed under vacuum and kept in an oil bath at 40 °C. The reaction lasted for 15 min and quenched in liquid nitrogen. Subsequently, the reaction mixture was diluted with THF, passed through a neutral alumina column. L-PtBA-*b*-L-PMMA as white solid was obtained after thrice precipitation in *n*-hexane and dryness under vacuum at room temperature for 24 h.

Yield: 2.72 g, $M_{n,GPC} = 18,000$, PDI = 1.20. FTIR: $v(-C(CH_3)_3)$: 1369 cm⁻¹; v(-C=0): 1728 cm⁻¹; v(C-C-0): 1191 cm⁻¹. ¹H NMR (CDCl₃) δ : proton in tirazole ring (7.73); triazole-CH₂-O-C=O (5.24); CH₃-CH₂-O-C=O, -CH₂-CH-triazole (4.01); -CH₂-CH-C=O (2.15); Br-C-(CH₃)₂ (1.86); -CH₂-CH-C=O, O-C(CH₃)₃ (1.85-1.22); CH₃-CH₂-O-C=O (1.19); O=C-C- (CH₃)₂ (1.06).

L-PtBA-*b*-L-PMMA (1.102 g, 0.06 mmol) and CH_2Cl_2 (20 mL) were added into a 100-mL round-bottomed flask. After complete dissolution, trifluoroacetic acid (TFA, 3 mL) was added. After standing at ambient temperature for 2 days, CH_2Cl_2 and TFA were removed under low vacuum. The crude product was dissolved in THF and precipitated in *n*-hexane for three times. After dryness under vacuum at ambient temperature for 24 h, L-PAA-*b*-L-PMMA was obtained.

Yield: 0.82 g. FTIR: v(-C=0): 1728 cm⁻¹; v(C-C-0): 1191 cm⁻¹. ¹H NMR (DMF- d_7) δ :-COOH (12.69); -CH₂-CH-C=0 (2.48); -CH₂-CH-C=0, -CH₂-C-C=0 (1.89); CH₃-C-C=0 (0.60-1.20).

Synthesis of L-PAA-b-G1-PMMA and L-PAA-b-G2-PMMA

A dry Schlenk flask was charged with L-PtBA-N₃ (3.2 g, 0.7 mmol), PBMP (0.4927 g, 1.05 mmol), PMDETA (0.1820 g, 1.05 mmol), and DMF (20 mL). After three freeze-pump-thaw cycles, CuBr (0.1507 g, 1.05 mmol) was added. Then the flask was kept in an oil bath preheated at 40 °C and the reaction lasted for 12 h. Subsequently, the reaction mixture was diluted with THF, passed through a neutral alumina column. Afterward, the mixture was concentrated by rotary evaporation and precipitated in methanol/water (50/50; v/ v) for three times and dried under vacuum to obtain L-PtBA-PBMP with two ATRP initiation sites. Yield: 2.62 g.

The synthesis of L-PtBA-*b*-G1-PMMA was carried out as follows. A 50-mL Schlenk flask charged with PtBA-PBMP (1.6 g, 0.32 mmol), MMA (22.9 g, 228.7 mmol), PMDETA (111.0 mg, 0.64 mmol), and THF (4 mL) was degassed by three freeze-pump-thaw cycles. Then, CuBr (91.8 mg, 0.64 mmol) was added and the flask was kept in an oil bath at 40 °C for 15 min. Subsequently, the reaction was stopped by dipping the flask in liquid nitrogen. The reaction mixture was diluted with THF, passed through a neutral alumina column. After rotary evaporation, thrice precipitation in *n*-hexane, and dryness under vacuum, the product was obtained as powder.

Yield: 6.68 g, $M_{n,GPC} = 24,000$, PDI = 1.20. FTIR: $\nu(-C(CH_3)_3)$: 1369 cm⁻¹; $\nu(-C=0)$: 1728 cm⁻¹; $\nu(C-C=0)$: 1191 cm⁻¹. ¹H NMR (CDCl₃) δ : $-OCH_3$ (3.53); $-CH_2-CH-C=0$ (2.15); $-CH_2-CH-C=0$ (1.98-1.64); $O-C(CH_3)_3$ (1.37); $CH_3-C-C=0$ (0.38-1.08).

The synthesis of L-PtBA-*b*-G2-PMMA follows the same procedure as the preparation of L-PtBA-*b*-G1-PMMA, such as the azidation of bromo end-groups of L-PtBA-*b*-G1-PMMA-Br, click reaction of L-PtBA-*b*-G1-PMMA-N₃ with PBMP and final ATRP of MMA with L-PtBA-*b*-G1-PMMA-PBMP as the macroinitiator.





SCHEME 2 Synthesis of linear diblock copolymer of L-PAA-b-L-PMMA. [Color figure can be viewed at wileyonlinelibrary.com]

$$\begin{split} M_{n,GPC} &= 28,400, \text{ PDI} = 1.21. \text{ FTIR: } \nu(\text{--C(CH}_3)_3): 1369 \text{ cm}^{-1}; \\ \nu(\text{--C=-0}): 1728 \text{ cm}^{-1}; \quad \nu(\text{C}\text{--C}\text{--O}): 1191 \text{ cm}^{-1}. \text{ }^{1}\text{H} \text{ NMR} \\ (\text{CDCl}_3) \quad \delta : -\text{OCH}_3 \quad (3.53); \quad -\text{CH}_2\text{--CH}\text{--C=-0} \quad (2.15); \\ -\text{CH}_2\text{--CH}\text{--C=-0} \quad (1.98\text{--}1.64); \quad -\text{C(CH}_3)_3 \quad (1.37); \text{CH}_3\text{--C}\text{--C=-0} \\ (0.38\text{--}1.08). \end{split}$$

The hydrolysis of PtBA block in L-PtBA-*b*-G1-PMMA and L-PtBA-*b*-G2-PMMA was carried out by the same procedure as that for L-PAA-*b*-L-PMMA.

Self-assembly of Block Copolymers Through Different Mixing Dynamics

DMF was selected as the common solvent to dissolve the block copolymers and water as the selective solvent to induce the self-assembly.

The typical procedure for gentle variation in solvent selectivity was as follows. Copolymer solution (5.0 mL, 2 mg·mL⁻¹) in DMF was added into a glass vial equipped with a stirring bar after passing through a 0.45- μ m nylon filter. Under vigorous stirring, water (2.0 mL) was injected at 10 mL h⁻¹ by syringe pump. As for L-PtBA-*b*-G2-PMMA, mixed solvent (V_{water} : $V_{DMF} = 1$) was slowly injected to copolymer solution in DMF to avoid the precipitation. All of the self-assemblies were dialyzed against water for 3 days with dialysis membrane (cut-off molecular weight: 3500 g mol⁻¹) to remove DMF. Finally, polymer concentration of self-assembly dispersion was adjusted to 1 mg mL⁻¹.

Compared with the gentle variation in solvent selectivity, the abrupt variation in mixing dynamic was achieved by injecting copolymer/DMF solution into water at the rate of 10 mL h⁻¹. The concentration and volume of initial copolymer solution as well as water volume were the same as above. Finally, those self-assembly dispersions were adjusted to the concentration of 1 mg mL⁻¹.

Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Bruker VECTOR-22 IR spectrometer using KBr pellets. Proton nuclear magnetic resonance (¹H-NMR) analysis was performed on a Bruker DRX-300 NMR (300 MHz) instrument in CDCl₃ or DMF- d_7 at room temperature with tetramethylsilane as the internal standard. The morphology of selfassemblies was observed under transmission electron microscopy (TEM, Hitachi H-7650, 100 kV). In a typical protocol of preparing TEM samples, 5 µL thinned aqueous dispersion of the self-assemblies was deposited to copper grid. Then, water was evaporated naturally. The molecular weight and its distribution were determined by gel permeation chromatography (GPC) using Waters 1515 apparatus equipped with a refractive index detector (RI, Wyatt WREX-02), a multiangle LLS detector (MALLS, Wyatt DAWN EOS),



FIGURE 1 ¹H NMR spectra of L-PtBA-Br (A) and L-PtBA-PBiB (B) in CDCl₃. [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 2 ¹H NMR spectra of L-PtBA-*b*-L-PMMA in $CDCl_3$ (A) and L-PAA-*b*-L-PMMA in DMF-*d*₇ (B). [Color figure can be viewed at wileyonlinelibrary.com]

and three Waters Styragel columns (HR2, HR4, HR6). Measurements were performed in THF at the flow rate of 1 mL min⁻¹ at room temperature and the calibration was built on polystyrene standards.

RESULTS AND DISCUSSION

Preparation of L-PAA-b-L-PMMA

The synthesis procedure of L-PAA-*b*-L-PMMA is illustrated in Scheme 2. L-PtBA-Br was first obtained by ATRP of tBA with EBiB as initiator, then converted to PtBA-N₃ through the azidation of bromo end-group. Afterward, click reaction between PtBA-N₃ and PBiB produced the macroinitiator of L-PtBA-PBiB for ATRP of MMA.

 1 H NMR analysis was used to confirm the click reaction between L-PtBA-N₃ and PBiB. Figure 1(A) reveals NMR spectrum of L-PtBA-Br. The signal at 2.15 ppm (e) is ascribed to the methine group of PtBA and that at 1.22–1.95 ppm (f, d)





FIGURE 3 GPC curves of L-PtBA-Br, L-PtBA-*b*-L-PMMA, L-PtBA*b*-G1-PMMA, and L-PtBA-*b*-G2-PMMA. [Color figure can be viewed at wileyonlinelibrary.com]

originates from the overlapping of tertiary butyl group and methylene group of PtBA backbone. The signals at 1.19 ppm (a) and 1.06 ppm (c) come from the methyl group of EBiB residue and that at 4.01 ppm (b, g) is attributed to the overlapping of methylene protons from EBiB and the methine proton of tBA unit beside bromo end-group. The polymerization degree (DP) of tBA calculated from the integral height ratio of signal "e" to that of signal "b + g" (H_e/H_{b+g}) is 38.

As illustrated in Figure 1(B), after the click reaction of PtBA-N₃ with PBiB, the characteristic signals of triazole proton at 7.73 ppm (h), methylene protons next to the electron-withdrawing triazole ring at 5.24 ppm (i) and methyl ptotons from PBiB at 1.86 ppm (j) appear. The integral height ratio of "H_i/H_{b+g}" is about 2:3. The above results suggest the successful synthesis of L-PtBA-PBiB.

Subsequently, L-PtBA-*b*-L-PMMA was prepared by ATRP of MMA using L-PtBA-PBiB macroinitiator. As shown in Figure 2(A), after the polymerization, the signal at 3.6 ppm (a') and the signal near 0.98 ppm (e') corresponding to the protons of methoxy group and α -methyl group of MMA unit appear.

The DP of PMMA block determined from the integral height ratio of " $H_{a'}/H_e$ " is 86. Furthermore, as revealed in Figure 3, GPC traces of L-PtBA-Br and L-PtBA-*b*-L-PMMA are narrow and unimodal. The elution time of L-PtBA-*b*-L-PMMA shifts to lower elution time compared with that of L-PtBA-Br, indicating the successful polymerization of MMA monomer. M_{n} , M_{vo} and PDI for both polymers are summarized in Table 1.

TABLE 1 Molecular Characteristics of L-PtBA-Br and L-PtBA-b-L-PMMA

Sample	M _{n,GPC}	$M_{\rm w,GPC}$	PDI	M _{n,NMR}
L-PtBA-Br	4600	5100	1.12	5100
L-PtBA-b-L-PMMA	18,000	21,600	1.20	13,800



FIGURE 4 FTIR spectra of L-PtBA-Br (A), L-PtBA-N₃ (B), L-PtBA-PBiB (C), L-PtBA-*b*-L-PMMA (D), and L-PAA-*b*-L-PMMA (E). [Color figure can be viewed at wileyonlinelibrary.com]

Figure 4 reveals FTIR spectra of L-PtBA-Br, L-PtBA-N₃, L-PtBA-PBiB, L-PtBA-*b*-L-PMMA, and L-PAA-*b*-L-PMMA. The peak at the wavenumber of 1369 cm⁻¹ is assigned to the characteristic symmetric stretching vibration of tertiary butyl from PtBA. Compare Figure 4(A) with Figure 4(B), it can be found that, after the azidation of PtBA-Br, characteristic absorbance at 2114 cm⁻¹ attributed to azido group appears, demonstrating the successful substitution of bromine group. After the click reaction with PBiB, this absorbance signal disappears due to the conversion of azido group into triazole

ring. As shown in Figure 4(D), the absorbance at 1277 cm⁻¹ and 1190 cm⁻¹ can be assigned to the symmetrical deformation vibration of α -methyl group and asymmetrical stretching vibration of C—C—O group of PMMA, respectively, which also reveals the introduction of PMMA block. After the selective hydrolysis to remove *tert*-butyl group from L-PtBA block, L-PAA-*b*-L-PMMA was finally obtained. Comparing Figure 4(D) with Figure 4(E), it is easy to find that the characteristic signal of symmetric stretching vibration of tertiary butyl at 1369 cm⁻¹ disappears after the selective hydrolysis. As well, a broad peak from 3500 cm⁻¹ to 2300 cm⁻¹ attributed to carboxylic acid groups appears.

The selective hydrolysis was also confirmed by ¹H NMR analysis as shown in Figure 2(B). The appearance of new signal at 12.69 ppm (f) can be attributed to the proton of newly formed carboxylic group. Meanwhile, the signal at ~1.60 ppm (d + d'), resulting from the methylene protons of polymer backbone, decreased dramatically due to the removal of *tert*-butyl group. The relative integral heights of the signal at 12.69 ppm and that at 0.60–1.20 ppm (H_f and H_e') is consistent with quantitative hydrolysis.

Preparation of L-PAA-b-G1-PMMA and L-PAA-b-G2-PMMA

Scheme 3 reveals the whole synthesis procedure of L-PtBA*b*-G1-PMMA and L-PAA-*b*-G2-PMMA. To ensure the well control over ATRP of MMA, the bromo end-groups of L-PtBA-Br and L-PtBA-*b*-G1-PMMA-Br were converted into azido groups, followed with the introduction of tertiary bromo at the corresponding macro-initiators such as L-PtBA-PBMP for L-PtBA-*b*-G1-PMMA and L-PtBA-*b*-G1-PMMA-PBMP for L-



SCHEME 3 Synthetic route to linear block dendritic copolymers of L-PtBA-*b*-G1-PMMA and L-PAA-*b*-G2-PMMA. [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 5 ¹H NMR and FTIR spectra of L-PtBA-PBMP. [Color figure can be viewed at wileyonlinelibrary.com]

PtBA-b-G2-PMMA through azide–alkyne click reaction between the AB₂ type initiator of PBMP and the related precursor.

Figure 5 exhibits ¹H NMR and FTIR spectra of L-PtBA-PBMP. As seen in Figure 5(A), after the click reaction, the characteristic signal of triazole ring at 7.72 ppm (h) appears. The new signals of methylene protons adjacent to the electron-withdrawing triazole ring at 5.20 ppm (i), methylene protons from PBMP residue [$-C(CH_2OCO)_2-$] at 4.27 ppm (j) and methyl protons from PBMP residue [$-CBr(CH_3)_2$] at 1.82 ppm (k) are also verified. The integral height ratio of "H_{b+g}/H_i" is close to 1.5 and is consistent with chemical structure. As for FTIR spectrum, the disappearance of stretching absorbance of azido group at 2114 cm⁻¹ clarifies the complete reaction of L-PtBA-N₃. All the above results confirm the successful preparation of L-PtBA-PBMP.

Then, ATRP of MMA monomer was carried out using L-PtBA-PBMP as the macroinitiator. To avoid chain coupling, the temperature was controlled at 40 $^\circ C$ and the reaction lasted





FIGURE 6 ¹H NMR spectra of L-PtBA-*b*-G1-PMMA (A) and L-PtBA-*b*-G2-PMMA (B) in CDCl₃. [Color figure can be viewed at wileyonlinelibrary.com]

for 15 min. As shown in Figure 6(A), after ATRP of MMA monomer, the signals of $-OCH_3$ at 3.53 ppm (a') and $-CH_3$ at 0.38–1.08 ppm (e') originated from PMMA appear. In the case of L-PtBA-*b*-G2-PMMA [Fig. 6(B)], the integral height ratio of signal e to signal a' (H_e/H_{a'}) decreases due to the formation of the second generation of PMMA dendron.

The subchain length of G1-PMMA (DP_{G1}) was determined as follows. The integral height of signal f (H_f) was set as 342, and the integral height of signal a^\prime (H_{a^\prime}) was automatically given as 532. Thus, DP_{G1} was calculated to be about 89 based on $H_{a'}/6$. When it came to DP_{G2} , H_f was set as 342, and $H_{a'}$ was automatically given as 1864. Thus, DP_{G2} was obtained to be 110 based on $(H_{a'} - 6DP_{G1})/12$. The successful preparation of L-PtBA-b-G1-PMMA and L-PtBA-b-G2-PMMA was further confirmed by GPC technique as shown in Figure 3. Their GPC traces are symmetrically narrow and keep moving to lower elution time with the increase in dendron generation, indicating the well-defined and expected chain structure. Molecular weight information obtained by GPC and NMR analysis are summarized in Table 2. As can be seen, $M_{n,GPC}$ and $M_{n,NMR}$ of L-PtBA-*b*-G1-PMMA are similar, while those of L-PtBA-b-G2-PMMA deviate from each other. This phenomenon can be explained by the following reasons. GPC characterization obtains the results based on the elution volume and the calibration was built using linear polystyrene standards in this work.

TABLE 2 Molecular Characteristics of L-PtBA-*b*-G1-PMMA and

 L-PtBA-*b*-G2-PMMA

Samples	M _{n,GPC}	M _{w,GPC}	PDI	M _{n,NMR}
L-PtBA-b-G1-PMMA	24,000	28,900	1.20	23,300
L-PtBA-b-G2-PMMA	28,400	34,500	1.21	68,200



FIGURE 7 ¹H NMR spectra of L-PAA-*b*-G1-PMMA (A) and L-PAA-*b*-G2-PMMA (B) in DMF-*d*₇. [Color figure can be viewed at wileyonlinelibrary.com]

As dendritic polymer has more compact conformation compared with its linear counterpart, so its hydrodynamic radius is relatively smaller and its elution volume from GPC is simultaneously shorter, making its $M_{n,GPC}$ relatively smaller, especially when the dendron generation is higher. Therefore, $M_{n,NMR}$ is calculated from the integration height, which is strictly proportional to the proton number.

The hydrolysis of tert-butyl group was performed by treating L-PtBA-b-G1-PMMA and L-PtBA-b-G2-PMMA with trifluoroacetic acid. Figure 7(A) exhibits ¹H NMR spectrum of L-PAAb-G1-PMMA.

The appearance of the signal at 12.72 ppm (f) attributed to the carboxylic group of PAA as well as the disappearance of the signal ascribed to the tertiary butyl group of PtBA establishes the successful preparation of L-PAA-*b*-G1-PMMA. Figure 7(B) reveals ¹H NMR spectrum of L-PAA-*b*-G2-PMMA, the signal at 12.72 ppm (f) also shows up. By comparison, the integral height ratio of "H_f/H_e'" decreases owing to the increase in PMMA dendron generation. Figure 8 illustrates FTIR spectra of different linear-block-dendritic copolymers. As seen in Figure 8(B), a characteristic stretching peak of azido group appears at 2119 cm⁻¹ after the azidation. When L-PtBA-*b*-G1-PMMA-PBMP was prepared, this signal disappears, verifying that the AB₂ initiator of PBMP has been linked to the chain ends of L-PtBA-*b*-G1-PMMA.

In addition, the disappearance of the characteristic symmetric stretching absorbance of tertiary butyl at 1369 cm⁻¹ and the appearance of broad absorbance from 3500 to 3200 cm⁻¹ attributed to hydroxyl groups of PAA, as well as the broadening of the stretching absorbance around 1730 cm⁻¹ owing to the overlapping of the absorbance signals of ester carbonyl groups of PMMA and carboxylic acid groups of PAA can confirm the successful hydrolysis of PtBA block.

In case of L-PtBA-*b*-G2-PMMA and L-PAA-*b*-G2-PMMA, it is observed that the absorbance at 1191 $\rm cm^{-1}$ assigned to the asymmetrical stretching vibration of C—C—O groups of

PMMA increases in its intensity compared with Figure 8(A–C), while the absorbance of tertiary butyl of PtBA at 1369 cm^{-1} decreases in its intensity, resulted from the formation of the second generation PMMA dendron. The broad absorbance of hydroxyl groups of PAA is also found in FTIR spectrum of L-PAA-*b*-G2-PMMA [Fig. 8(F)]. These aforementioned analyses indicate the successful preparation of L-PAA-*b*-G1-PMMA and L-PAA-*b*-G2-PMMA.

Self-assembly of L-PAA-*b*-L-PMMA, L-PAA-*b*-G1-PMMA, and L-PAA-*b*-G2-PMMA by Gentle Variation in Solvent Selectivity

Gentle variation in solvent selectivity to induce self-assembly of three block copolymer with different topologies was conducted by injecting water slowly into polymer solution in the common solvent. The self-assembly morphologies of



FIGURE 8 FTIR spectra of L-PtBA-*b*-G1-PMMA (A), L-PtBA-*b*-G1-PMMA-N₃ (B), L-PtBA-*b*-G1-PMMA-PBMP (C), L-PAA-*b*-G1-PMMA (D), L-PtBA-*b*-G2-PMMA (E), and L-PAA-*b*-G2-PMMA (F). [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 9 TEM images of the self-assemblies of L-PAA-*b*-L-PMMA (A), L-PAA-*b*-G1-PMMA (B), and L-PAA-*b*-G2-PMMA (C) prepared by gentle variation in solvent selectivity. [Color figure can be viewed at wileyonlinelibrary.com]

those block copolymers of L-PAA-*b*-L-PMMA, L-PAA-*b*-G1-PMMA, and L-PAA-*b*-G2-PMMA were observed under TEM.

As exemplified in Figure 9(A) (Supporting Information Fig. S3), L-PAA-b-L-PMMA self-assemblies are mainly spherical micelles with much small diameter (<10 nm), which further aggregated into caterpillar-like micelles with a diameter of about 30 nm. As for L-PAA-b-G1-PMMA shown in Figure 9(B) (Supporting Information Fig. S4), spherical micelles are also present but their diameter is larger (approximately 20 nm) and their number is much low. Meanwhile, much more and much longer caterpillar-like micelles are mostly observed. Besides the block length ratio of amphiphilic block copolymers,³³ the topology difference of Y-type block copolymer from linear diblock copolymer also contributes to the variation in their self-assembly morphologies.³⁴ In the case of L-PAA-b-G2-PMMA, spherical micelles and caterpillar-like micelles with different length were formed, as shown in Figure 9(C) (Supporting Information Fig. S5). Compared with Figure 9(B), the caterpillar-like micelles of L-PAA-b-G2-PMMA are rather twisted in shape and large in width, probably due to the increase in dendron generation.

Eisenberg and coworkers^{35,36} studied the self-assembly of linear polystyrene-b-PAA copolymers, revealing that micellelike aggregates were the primary morphology. Compared with polystyrene, PMMA is more hydrophilic and micible with PAA. Therefore, the spherical micelle size of L-PAA-b-L-PMMA in this case is much small. What is more, the spherical micelles should have the higher probability to grow into caterpillar-like micelles, whose diameter is several times larger than that of spherical micelles. This observation suggests that the caterpillar-like micelles of L-PAA-b-L-PMMA might be formed by aggregation of spherical micelles. Especially, we have studied the morphologies of L-PAA-b-L-PSt assemblies throughout RAFT dispersion polymerization.37 With the increase in the reaction time from 1 to 2 h and 9 h, the sequence of the morphologies follows the order of spherical micelles, spherical/cylindrical micelles, and vesicle, convincing us to believe that the cylindrical micelle should be derived from spherical micelles and the vesicle should be derived from cylindrical micelles. In this work, the caterpillar-like micelles should be derived from spherical micelles. As for the self-assemblies of L-PAA-b-G1-PMMA and

L-PAA-*b*-G2-PMMA, the spherical micelles are relatively larger than those of linear block copolymer, caused by the topology change in PMMA component as well as its volume fraction. More crowded chain conformation and compact structure of G2-PMMA dendrons should force the chains repel to each other and increase the curvature simultaneously, resulting in the twist morphology of the selfassemblies of L-PAA-*b*-G2-PMMA.

It is worthy to notice that the image contrast of spherical micelles is deeper than that of caterpillar-like micelles in Figure 9(B,C), indicating the variation in chain package density in the micelle cores.³⁸ While the image contrast of spherical micelles and caterpillar-like micelles is almost the same in Figure 9(A), PMMA linear blocks might be normally packed in both cases. A possible explanation for this observation might be as follows. From L-PAA-b-L-PMMA, L-PAA-b-G1-PMMA to L-PAA-b-G2-PMMA, the hydrophobic component of PMMA changes its topology from linear, Y-type to dendron. Moreover, the equilibrium morphology of the obtained micelle should keep the minimum value of interfacial free energy.³⁷ As the interfacial tension between PMMA core and PAA shell is constant, the interfacial area should be dominative. Therefore, in the spherical micelle formation of L-PAA-b-G1-PMMA and L-PAA-b-G2-PMMA with PMMA dendron, more PMMA chains tend to densely pack to form the core, lessening the interfacial area and further interfacial free energy.

However, high compactness of chain packing is accompanied with the increase of curvature,³⁹ leading to the increase in interfacial free energy. Therefore, in the formation of caterpillar-like micelles, less PMMA chains would be packed to the core, leading to the low packing density. The nonlinear topology of PMMA chains in G1-PMMA and G2-PMMA is also responsible for the loose packing because those PMMA chains are little difficulty to fold and interpenetrate with each other.⁴⁰ Thus, the image contrast of caterpillar-like micelles is low in Figure 9(B,C).

Self-assembly of L-PAA-*b*-L-PMMA, L-PAA-*b*-G1-PMMA, and L-PAA-*b*-G2-PMMA by Abrupt Variation in Solvent Selectivity

Along with the influence of dendron generation on the morphology of self-assemblies, the mixing dynamics could also





FIGURE 10 TEM images of the self-assemblies of L-PAA-*b*-L-PMMA (A), L-PAA-*b*-G1-PMMA (B), and L-PAA-*b*-G2-PMMA (C) prepared by abrupt variation in solvent selectivity. [Color figure can be viewed at wileyonlinelibrary.com]

take their effect. The self-assemblies have been prepared by abrupt variation in solvent selectivity, where the amphiphilic copolymer solution in DMF was injected slowly to the nonsolvent of water. The concentration and volume of polymer solution as well as the volume of water are the same as the gentle variation in solvent selectivity.

As can be observed in Figure 10, in comparison with the gentle variation in solvent selectivity, the self-assemblies prepared by abrupt variation in solvent selectivity are mostly spherical micelles along with the presence of short and little caterpillar-like micelles. Slow addition of polymer solution into water caused the abrupt variation in solvent quality and endowed the polymer chains the higher possibility of the intramolecular association.²⁷ Therefore, amphiphilic PAA/ PMMA block copolymers would first undergo the intramolecular collapse of PMMA segments, then several collapsed block copolymers aggregated into the micelle-like self-assemblies, whose diameter is much larger than that of spherical micelles in Figure 9(A). Meanwhile, the abrupt variation in solvent quality made it very difficult for polymer chains to achieve the thermodynamically favored state of selfassemblies and left much lower possibility for the collapsed block copolymers to grow into long and straight caterpillarlike micelles. Thus, in this case of abrupt variation in solvent quality, only short and twisted caterpillar-like micelles were observed for L-PAA-b-L-PMMA and L-PAA-b-G1-PMMA (Fig. 10; Supporting Information Figs. S6 and S7). As for the selfassemblies of L-PAA-b-G2-PMMA prepared by abrupt variation in solvent selectivity, dendritic topology leads to relatively compacted chain conformation of G2-PMMA dendrons, making them much more difficult to form caterpillar-like micelles. Thus, spherical micelles with about 20 nm diameter but no caterpillar-like micelles are found as shown in Figure 10(C) (Supporting Information Fig. S8).

CONCLUSIONS

PAA and PMMA block copolymers with different topologies such as double linear blocks, PAA linear block/PMMA G1dendron, and PAA linear block/PMMA G2-dendron were successfully prepared by the combination of ATRP and the azide–alkyne click reaction. The influence of dendron generation as well as mixing dynamics on the self-assembly was

association and allowed the associates to grow into longer caterpillar-like micelles, while abrupt variation in solvent selectivity favored the intramolecular association and inhibited the associates to grow further. As well, with the increase in dendron generation to G2, PMMA component in different block copolymers became more compact, leading to the twisting of caterpillar-like micelles in the case of gentle variation in solvent selectivity and no formation of caterpillar-like micelles in the case of abrupt variation in solvent selectivity.
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investigated in detail. In the self-assembly induced by gentle

variation in solvent selectivity, with the increasing dendron

generation from L-PAA-b-L-PMMA to L-PAA-b-G2-PMMA, the

main morphology of the self-assemblies changes from the

spherical micelles, straight caterpillar-like micelles to twisted

caterpillar-like micelles, consistent with the stiffness of PMMA component. The self-assembly via abrupt variation in

solvent selectivity produced mainly the spherical micelles

and lessoned the formation of caterpillar-like micelles with

the increase in PMMA dendron generation. The dependence

of self-assembly morphology on the PMMA dendron genera-

tion and variation in solvent selectivity should be attributed

to the chain compactness of PMMA component and the

dynamics to mix polymer solution with non-solvent. Gentle

variation in solvent selectivity enabled the intermolecular

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Polymer JOURNAL OF POLYMER SCIENCE Chemistry

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