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ORIGINAL PAPER

Synthesis of amphiphilic diblock copolymers by direct radical polymerization of acrylic acid via DPE method

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Abstract Amphiphilic diblock copolymers, poly(methyl methacrylate)-*b*-poly (acrylic acid) (PMMA-*b*-PAA) was prepared by 1,1-diphenylethene (DPE) method. First, free radical polymerization of methyl methacrylate was carried out with AIBN as initiator in the presence of DPE, giving a DPE-containing PMMA precursor with controlled molecular weight. Amphiphilic diblock copolymer PMMA-*b*-PAA was then prepared by radical polymerization of acrylic acid (AA) in the presence of PMMA precursor. The formation of PMMA-*b*-PAA was confirmed by ^{1}H NMR spectrum and gel permeation chromatography. Transmission electron microscopy and dynamic light scattering were used to detect the self-assembly behavior of the amphiphilic diblock polymers in methanol.

Keywords Living free radical polymerization · Amphiphilic diblock copolymers · Acrylic acid · Self-assembly · 1,1-Diphenylethene

Introduction

Amphiphilic block copolymers containing poly(acrylic acid) (PAA) segment have attracted increasing interests [1]. Traditionally, they were synthesized by sequential living anionic polymerization [2, 3] of protected monomers, such as *tert*-butyl acrylate (*t*BA), followed by hydrolysis. However, the anionic polymerization need to be carried out under rigorous conditions such as in high-vacuum, highly purified monomers, and solvents. Recently, controlled radical polymerizations such as stable free radical polymerization (SFRP), atom transfer radical polymerization (ATRP), and reversible addition fragmentation chain transfer polymerization (RAFT) have

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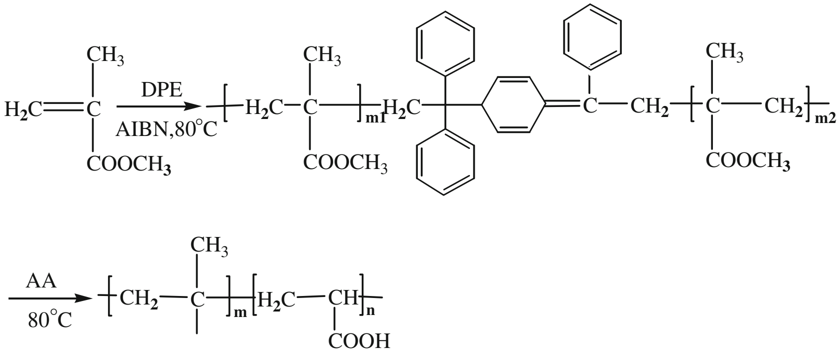


Scheme 1 Synthesis of amphiphilic diblock copolymer PMMA-*b*-PAA

become established methods to obtain block copolymer under mild conditions. Block copolymers containing PAA segments have been successfully synthesized by ATRP [4–11], RAFT [12–14], and SFRP [15, 16] techniques, or via combination of these controlled radical polymerization methods [17–19]. The iodide-mediated radical polymerization was also employed to prepare block copolymers containing PAA segment [20].

Since the DPE method was patented by Bremser [21, 22], especially since Nuyken's group [23] reported it in 2001 in the open scientific literature, there are a lot of papers on this novel controlled radical polymerization system [24–37]. It was found that conventional radical polymerizations became controlled if a small amount of 1,1-diphenylethene (DPE) was added. Its polymerization conditions are very close to those of conventional free radical polymerization and there is no use of any catalyst as those in ATRP, which need to be removed, or no use of expensive agents as those in SFRP and RAFT. The DPE method appears to be a useful alternative to prepare block copolymers. Despite many kinds of block copolymers have been prepared by the DPE method up to the present, there is still no report on the synthesis of poly(methyl methacrylate)-*b*-poly(acrylic acid) (PMMA-*b*-PAA) block copolymers using this method. In this article, we utilized the DPE method to prepare PMMA-*b*-PAA through the following two steps as shown in Scheme 1 [30, 32]. First, free radical polymerization of methyl methacrylate was carried out with AIBN as initiator in the presence of DPE, giving a PMMA precursor with controlled molecular weight. Second, free radical polymerization of acrylic acid (AA) was carried out in the presence of PMMA precursor and amphiphilic diblock copolymer PMMA-*b*-PAA was obtained directly.

Experimental

Materials

MMA (>99%) and AA (>99%) were all from Beijing Chemical Reagent Co. MMA was dried over CaH_2 (Aldrich, 90–95%) overnight, and then distilled under reduced pressure. AA was dried over $MgSO_4$ for 24 h, and then distilled under reduced pressure. 2,2′-Azobis(isobutyronitrile) (AIBN, 98%, Fluka) was recrystallized from ethanol. DPE was synthesized according to the method reported by Anschütz and Hilbert [38] and distilled under reduced pressure. All other reagents were used as received without any further purification.

Characterization

Monomer conversion was obtained gravimetrically. Molecular weights and molecular weight distributions of the polymers were measured using a Tosoh HPLC 8220 gel permeation chromatography (GPC) (column: TSK-Gel Super HZM-M×2) with THF as the eluent (40 °C) at a flow rate of 0.35 mL/min. Narrow polystyrene standards were used to generate the calibration curve. ^1H NMR spectra were recorded on a Bruker AV600-MHz NMR spectrometer. $CDCl_3$ or CD_3COCD_3 was used as the solvent. Dynamic light scattering measurement was done by using Brookhaven BI-200SM operated at 532 nm at an angle of 90° at 25 °C. Emulsions for light scattering measurement were prepared by putting block copolymer samples into previously filtered and distilled methanol directly. After being stirred for about 1 h or being treated under ultrasonic wave for a few minutes, stable emulsion was obtained. All the emulsions were filtered through a 0.45 μm filter before analysis. Transmission electron microscopy (TEM) was carried out on a Hitachi H-800 microscope operated at an acceleration voltage of 200 kV. Samples were prepared by dropping a droplet of emulsion (formed by self-assembly of block copolymers in methanol) on a copper TEM grid, which was coated with thin films of Formvar and carbon successively, and methanol was let to evaporate under ambient atmosphere for 1 h.

Preparation of PMMA precursor

In a typical experiment, 10.0 g (100 mmol) of MMA, 65.6 mg (0.4 mol% to MMA) of AIBN and 108 mg (0.6 mol% to MMA) of DPE were added into a 100 mL dry round-bottom flask equipped with a magnetic stirrer and degassed by five freeze–pump–thaw cycles. The polymerization was carried out at 80 °C. After polymerization, the polymer was obtained by precipitation in methanol, and purified by dissolution/precipitation from chloroform into methanol.

Preparation of PMMA-*b*-PAA by radical polymerization of AA in the presence of PMMA precursor

In a typical experiment, 0.5 g of the PMMA precursor ($M_{n,\ \mathrm{GPC}} = 10{,}400$, $M_w/M_n = 1.34$), 2.5 g (34.7 mmol) of AA and 20 mL of 1,4-dioxane were added to a 50 mL dry round-bottom flask equipped with a magnetic stirrer. After five freeze–pump–thaw cycles, the flask was placed in an oil bath thermostated at 80 °C. The polymerization was stopped by pouring the reaction mixture into a large amount of cold cyclohexane.

Results and discussion

Preparation of PMMA precursor

The free radical polymerization in the presence of DPE has been investigated by Nuyken's and Bresmer's groups. In this system, DPE reacted with growing chains and the activity of growing chain radicals reduced. Combination termination of two DPE-ended radicals formed a unique semiquinoid structure as shown in Scheme 2 [30, 32].

In our experiment, 20 g (0.2 mol) of MMA was polymerized in bulk at 80 °C in the presence of DPE with AIBN as the initiator. The molar ratio of AIBN to MMA was 0.004:1, and that of AIBN to DPE was 2:3. After 3 h, the reaction mixture was poured into cold methanol to stop the polymerization. The ^{1}H NMR spectrum of the purified PMMA is shown in Fig. 1.

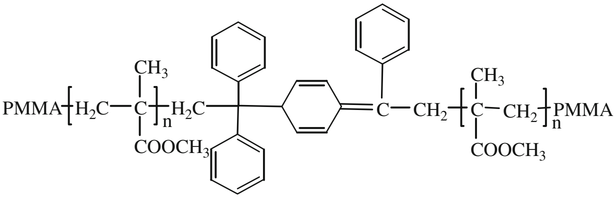
As shown in Fig. 1, in addition to the large absorptions of the protons of main chain repeating units from 1.2 to 2.0 ppm and that of methoxyl protons at 3.6 ppm, the polymer also shows the characteristic signals of the phenyl protons at 7.0–7.5 ppm and the protons of semiquinoid ring at 5.4–6.1 ppm. On the assumption that one polymer chain contains one semiquinoid structure and taking the molecular weight of the semiquinoid unit into consideration, the number average molecular weight of PMMA precursor can be calculated from the peak intensity ratio of the phenyl protons to methoxyl protons using the following equation.

$$M_{n,\mathrm{NMR}} = 100 \times 5I_{\mathrm{d}}/I_{\mathrm{b}} + 360 = 9,860$$

where I_{d} and I_{b} are the integral values of phenyl protons and methoxyl protons, respectively, 100 and 360 are the molecular weight of MMA and semiquinoid unit, respectively. This value was in good agreement with that obtained by GPC, confirming that there was indeed one semiquinoid structure in each polymer chain.

Preparation of PMMA-*b*-PAA by radical polymerization of AA in the presence of PMMA precursor

According to the mechanism proposed in [30, 32], the formation of block copolymers by DPE method was a two-step process. In the first step, a precursor polymer containing semi-quinoid structure was prepared in the presence of small amount of DPE. This precursor polymer was used as active specie in the second polymerization



Scheme 2 Semiquinoid structure of PMMA precursor

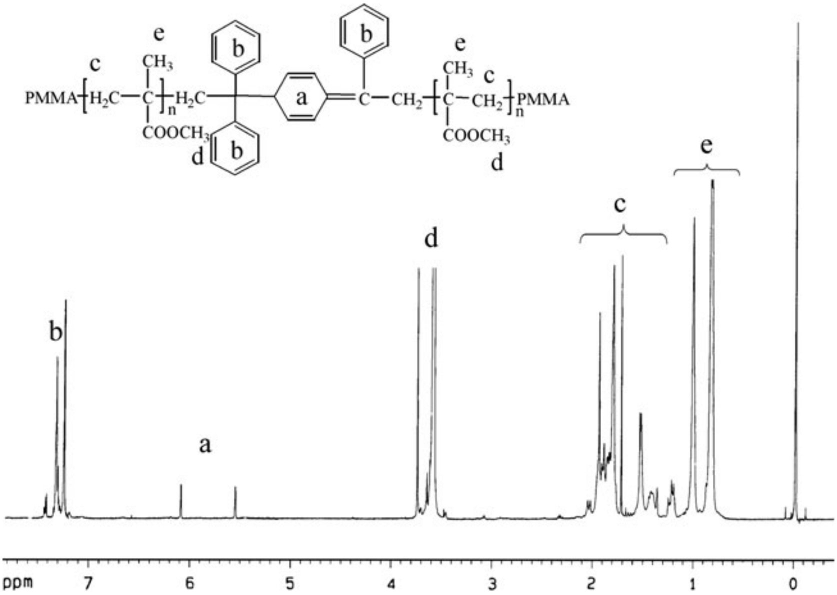
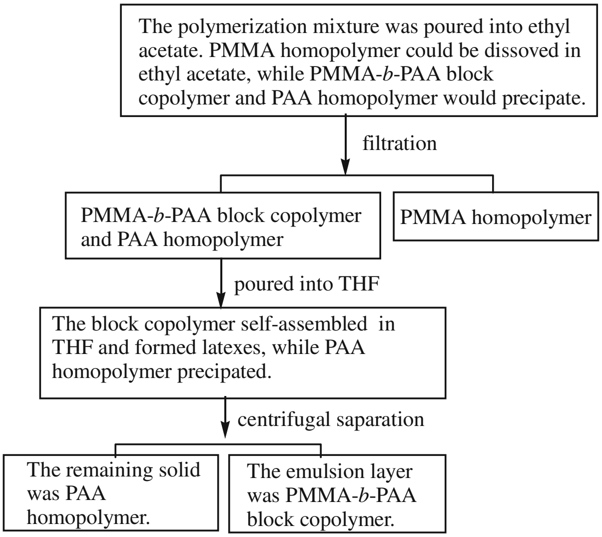


Fig. 1 ^{1}H NMR spectrum of PMMA precursor ($M_{n,\ \mathrm{GPC}} = 10{,}400$, $M_w/M_n = 1.34$). Solvent: $CDCl_3$. For detailed preparation conditions, see the text

process. The block copolymer formation started when the semiquinoid structure of precursor polymer was attacked by the growing radical. The attack of growing radicals would lead to the decomposition of the semiquinoid structure, and at the same time block copolymer and DPE ended macro-radical would be generated. The DPE ended macro-radical was inactive and could not initiate the polymerization of the second monomer. However, the semiquinoid structure precursor would be regenerated if the combination of two DPE ended macro-radicals take place. When all the PMMA precursor or DPE ended macro-radical were consumed up, homopolymer of the second monomer would be obtained.

In our study, the polymerization of AA in the presence of PMMA precursor was carried out in 1,4-dioxane at 80 °C. No initiator was added and the polymerization of AA might be initiated by thermal initiation. The polymerization system became milky after 15 min, indicating that the polymerization of AA took place because PAA could not dissolved in 1,4-dioxane at 80 °C. With the increase of AA conversion, the polymerization system became more and more turbid. However, no precipitate could be detected in this system. After polymerization, the polymerization system became transparent when it was cooled down below 70 °C. The PMMA-*b*-PAA block copolymer was purified by the following separation procedure (Scheme 3).

In the reaction system consisting of 0.5 g of PMMA precursor ($M_{n,\ \mathrm{GPC}} =$ 10,400, $M_w/M_n = 1.34$), 2.5 g of AA, and 20 g of 1,4-dioxane, the monomer conversion reached 30% in 6 h. At this conversion, a small amount of PMMA precursor (0.095 g) still existed and no PAA homopolymer could be detected. When



The polymerization mixture was poured into ethyl acetate. PMMA homopolymer could be dissoved in ethyl acetate, while PMMA-*b*-PAA block copolymer and PAA homopolymer would precipate.

PMMA-*b*-PAA block copolymer and PAA homopolymer

PMMA homopolymer

The block copolymer self-assembled in THF and formed latexes, while PAA homopolymer precipated.

The remaining solid was PAA homopolymer.

The emulsion layer was PMMA-*b*-PAA block copolymer.

Scheme 3 The purification process for PMMA-*b*-PAA block copolymer

the reaction time was 12 h, the monomer conversion reached 85%. At this conversion, nearly no PMMA precursor could be detected and about 1.87 g of block copolymer PMMA-*b*-PAA (A) were obtained. However, 0.75 g of PAA homopolymer was also found, indicating that all the PMMA precursor was exhausted to form PMMA-*b*-PAA block copolymer.

In most reports for the synthesis of block copolymers, the successful formation of block copolymers was usually confirmed by comparing the GPC curve of block copolymer with that of the first block. However, in this study, PMMA-*b*-PAA block copolymer was not soluble in THF, especially when PAA block was longer enough. Therefore, we tried to transform PAA block into poly(methyl acrylate) (PMA) block by esterification of PAA block with methanol. The typical esterification procedure was as follows. 0.5 g of PMMA-*b*-PAA (A), 0.618 g (3 mmol) of dicyclohexylurea (DCC), 22.4 mg (0.1834 mmol) of 4-(dimethylamino) pyridine (DMAP), 2.0 g of methanol, and 20 mL of 1,4-dioxane were added to a 50 mL dried round-bottom flask equipped with a magnetic stirrer. The solution was stirred at room temperature under argon. After 48 h, the precipitated dicyclohexylurea was filtered off and the filtered solution was condensed with rotatory evaporation. PMMA-*b*-PMA diblock copolymer was obtained by precipitation in a large amount of methanol and then dried under vacuum.

Comparison of IR spectrum (not shown) of PMMA-*b*-PAA diblock copolymer with that of its esterified product PMMA-*b*-PMA showed that the broaden absorption at 3000 cm^{-1} due to the carboxyl group of PAA block disappeared almost completely and the absorption at 1707 cm^{-1} shifted to 1730 cm^{-1}, indicating that PMMA-*b*-PAA copolymer had been transformed into PMMA-*b*-PMA copolymer successfully.

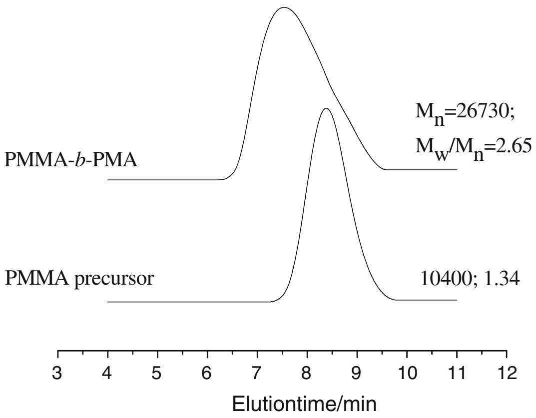


Fig. 2 GPC curves of PMMA precursor and PMMA-*b*-PMA block copolymer (PMMA-*b*-PMA was esterification product of the purified PMMA-*b*-PAA)

The GPC curves of the esterification product of PMMA-*b*-PAA and PMMA precursor are shown in Fig. 2. It can be seen that the molecular weight distribution shifted to higher molecular weight direction compared with the PMMA precursor although there was a small tail at lower molecular weight direction, indicating the successful formation of PMMA-*b*-PAA block copolymer.

The length of PAA block could be simply controlled by changing the concentration of AA. For example, in the blocking polymerization stage, 0.5 g of PMMA precursor ($M_{n,\ \mathrm{GPC}} = 10{,}400$, $M_\mathrm{w}/M_n = 1.34$) and 20 mL of 1,4-dioxane were still used, but the amount of AA was reduced from 2.5 to 1.0 g. The polymerization was also carried out at 80 °C for 12 h. The AA conversion reached 75%. After purification, 0.15 g of PAA homopolymer and 1.1 g of block copolymer PMMA-*b*-PAA (B) were obtained, while no PMMA homopolymer could be detected. The number average molecular weight and the amount of PMMA precursor were the same as those in the above experiment, so the length of PAA block must be shorter at the lower AA concentration.

Self-assembly behavior of PMMA-*b*-PAA in methanol

PAA homopolymer could be dissolved in methanol, but methanol was nonsolvent for PMMA homopolymer. Hence, the block copolymer PMMA-*b*-PAA could self-assemble in methanol to form latexes like emulsion. Furthermore, the PAA block should form the shell layer and the PMMA block should be sheltered in the core because of the different dissolving property of the PMMA and PAA segments. The ^{1}H NMR (Fig. 3) spectrum of the block copolymer in methanol showed that the characteristic signals of methyl protons (0.85, 1.02 ppm) and methoxyl protons (3.60 ppm) for PMMA were very weak as compared with that in $CDCl_3$. This provided direct evidence for the self-assembly of PMMA-*b*-PAA block copolymer in methanol.

TEM and DLS were used to characterize the size and size distribution of the aggregates of the block copolymers in methanol. Two purified block copolymers PMMA-*b*-PAA (A) and PMMA-*b*-PAA (B) were investigated. Both block

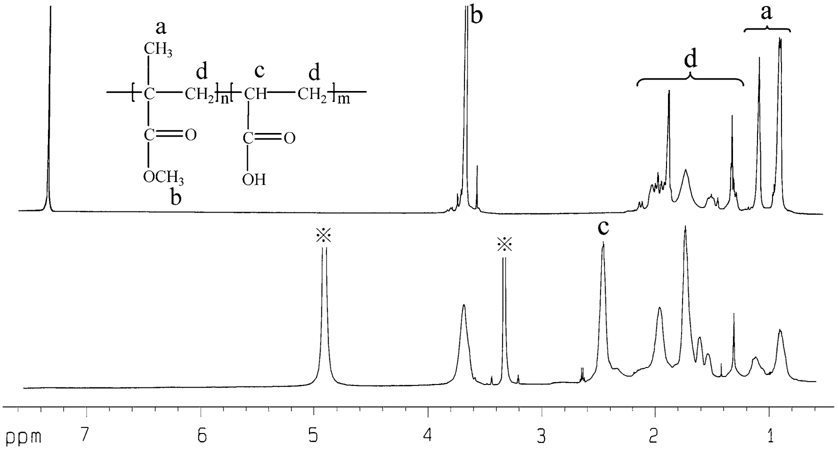


Fig. 3 ^{1}H NMR spectra of the purified PMMA-*b*-PAA (A) in CD_3OD (*bottom*) and $CDCl_3$ (*upper*), respectively. Attributed to CH_3OH and H_2O in CD_3OD

Table 1 Details about block copolymers PMMA-*b*-PAA (A) and PMMA-*b*-PAA (B)

Sample	PMMA precursor (g)	Dioxane (mL)	AA (g)	Reaction time (h)	AA conversion (%)	PAA homopolymer (g)	PMMA-*b*-PAA (g)
A	0.5	20	2.5	12	85	0.75	1.87
B	0.5	20	1.0	12	75	0.15	1.10

copolymers were prepared with the same PMMA precursor ($M_{n,\ \mathrm{GPC}} = 10{,}400$, $M_w/M_n = 1.34$). The details about sample A and B are shown in Table 1.

The TEM images (Fig. 4) showed the typical morphology of PMMA-*b*-PAA aggregates in methanol. It can be seen that PMMA-*b*-PAA aggregates showed spherical shape.

The results of DLS are shown in Fig. 5. For PMMA-*b*-PAA (A), the number average diameter was 412 nm. For PMMA-*b*-PAA (B), the number average diameter was 298 nm.

Furthermore, the particle diameter of PMMA-*b*-PAA (A) in methanol was bigger than that of PMMA-*b*-PAA (B). It indicated that the particle size was mainly controlled by the length of PAA block when the length of PMMA block was the same.

Conclusion

PMMA-*b*-PAA block copolymer could be prepared successfully via direct polymerization of AA in the presence of PMMA precursor which was synthesized by DPE method. Furthermore, the length of PAA block could be controlled by

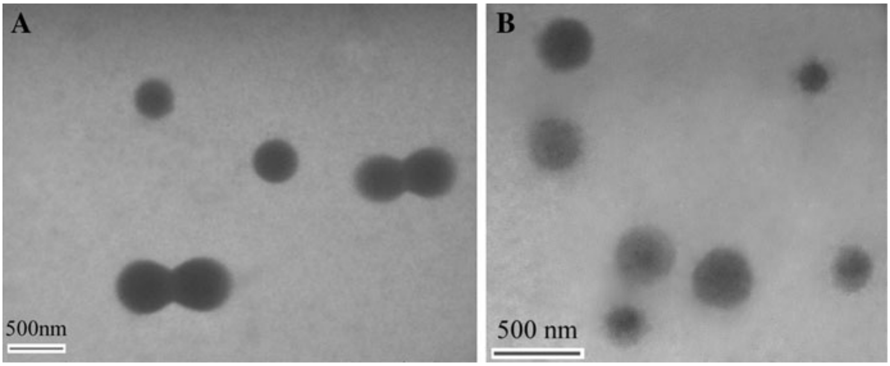


Fig. 4 TEM pictures for the particles formed by the PMMA-*b*-PAA in methanol. **A** PMMA-*b*-PAA, **B** PMMA-*b*-PAA

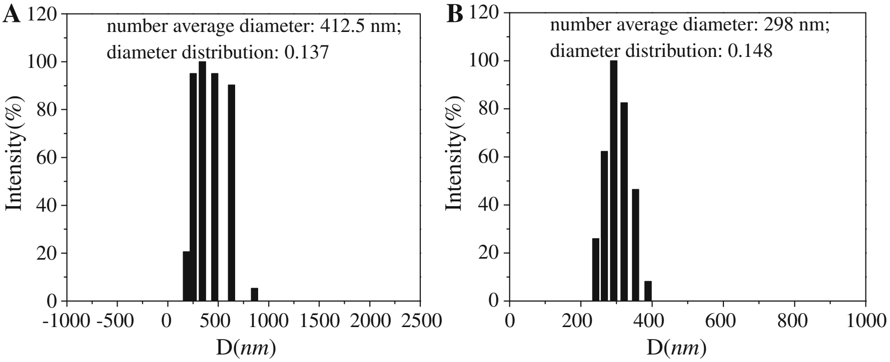


Fig. 5 Diameter distributions of the particles formed by PMMA-*b*-PAA in methanol. **A** PMMA-*b*-PAA, **B** PMMA-*b*-PAA

changing the concentration of AA in the blocking polymerization stage. The resulting block copolymers could self-assemble in methanol to form spherical aggregates.

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