

Self-assembly assisted polymerization (SAAP): approaching long multi-block copolymers with an ordered chain sequence and controllable block length

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A combination of polymer physics and synthetic chemistry has enabled us to develop self-assembly assisted polymerization (SAAP), leading to the preparation of long multi-block copolymers with an ordered chain sequence and controllable block lengths.

In the last two decades, block copolymers have attracted much attention in both polymer chemistry and physics because of their synthetic challenge and rich phase diagrams in bulk and in solution.^{1–5} The advancement of synthetic methods, such as ionic polymerization and various kinds of ‘living’ free-radical polymerization, has made the synthesis of narrowly distributed diblock and triblock copolymers possible. In theory, one could sequentially add different types of monomers into a living system to prepare long multi-block heteropolymer chains. In reality, each time the addition of new monomers introduces impurities and some of the reactive chain ends are terminated. This is why the success in this direction has been very limited. With much effort, the preparation of pentablock and octablock copolymers has been reported recently.^{6,7}

Alternatively, one could prepare narrowly distributed polymer blocks with their two ends reactive and then join them together to form long multi-block heteropolymer chains. This approach has been used to prepare polyurethanes, poly(ether ester)s and poly(ether amide)s. However, it should be noted that in these cases, the lengths of the blocks are normally short, typically with a molar mass less than 5000 g mol⁻¹. This is because the reaction rate decreases dramatically as the length of the block increases; namely, the reactive ends are wrapped and hidden inside the coiled chains in solution as well as fact that the concentration of the chain ends is too low. The reaction practically stops if the starting blocks or the chains are too long.

Therefore, it has been a difficult challenge in polymer chemistry to synthesize long multi-block heteropolymer chains with an ordered sequence and controllable block lengths. The significance of producing such long ordered multi-block heteropolymers could not be overestimated because they will not only provide unique systems for the study of polymer physics, but also lead to a new type of polymer materials.

The key to the success of the preparation of such a long multi-block copolymer is how to increase the concentration of the reactive ends of di- or tri-block copolymers and to effectively couple them together. It has been well known in polymer physics that the self-assembly of block copolymer chains in a selective solvent can form different core-shell micelle-like structures. With this in mind, one should be able to force the reactive ends to stay on the periphery or in the center of the micelle-like structure if the reactive functional groups were attached to the ends of the block copolymer chains.^{8–10} We report herein a novel synthetic methodology—self-assembly assisted polymerization (SAAP), for the synthesis of long multi-block copolymers with an ordered chain sequence and controllable block lengths, illustrated in Fig. 1.

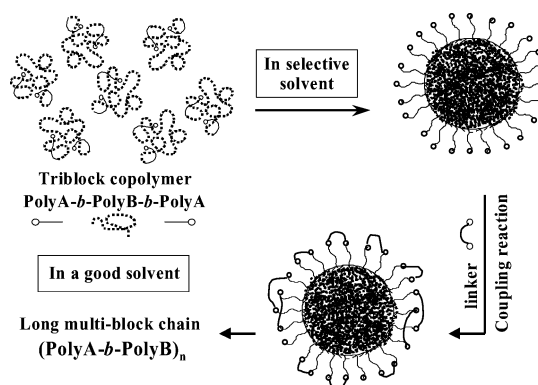


Fig. 1 Schematic of the self-assembly assisted polymerization (SAAP) of triblock copolymers in a selective solvent for the synthesis of long multi-block copolymers with an ordered chain sequence and controllable block lengths.

The functionalized triblock copolymer, (CICOCO)[poly(methyl methacrylate)-*b*-polystyrene-*b*-poly(methyl methacrylate)](COCOCI) ((CICOCO)[PMMA-*b*-PS-*b*-PMMA])(COCOCI) was prepared *via* anionic copolymerization followed by termination with an excess amount of oxalyl chloride (CICO-COCl).[†] M_w of the PMMA and PS blocks were 8.75×10^2 and 2.10×10^4 g mol⁻¹, respectively. Laser light scattering data showed that it was soluble in a solvent mixture of methyl acetate and acetonitrile (10/1, v/v) at 45 °C. As the temperature decreases, they could self-assemble into a core-shell micelle-like structure with a collapsed PS core and a swollen PMMA shell at room temperature. A peak located at 3–4 nm in $f(R_h)$ was observed, which represents individual triblock copolymer

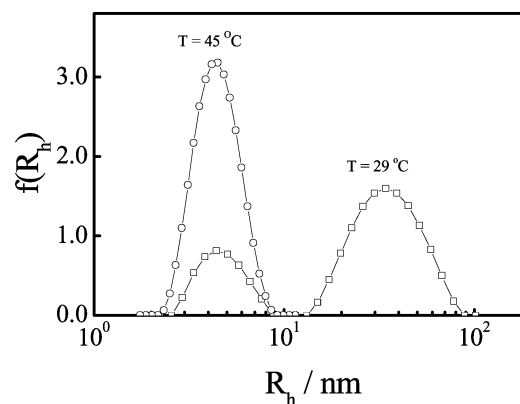


Fig. 2 Typical hydrodynamic radius distributions ($f(R_h)$) of individual triblock PMMA-*b*-PS-*b*-PMMA copolymer chains in a solvent mixture of methyl acetate and acetonitrile (10.0:1.0, v/v) at 45 °C and the aggregates formed *via* the self-assembly of the triblock copolymer chains at 29 °C, where the copolymer concentration is $\sim 1 \times 10^{-4}$ g mL⁻¹.

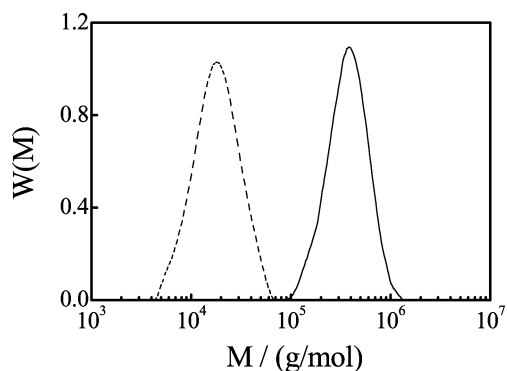


Fig. 3 Weight distributions of molar mass of triblock PMMA-*b*-PS-*b*-PMMA copolymer (dashed line) and long multi-block (PS-*b*-PMMA)_{*n*} heteropolymer (solid line), determined by size exclusion chromatography.

chains (Fig. 2). This peak was split into two at 29 °C, the second peak indicating the self-assembly of the triblock copolymer chains. Pentanediol (HO(CH₂)₅OH) was added as the linking agent to couple each two ends of the triblock copolymer chains *via* condensation in the presence of pyridine.[‡] The resultant multi-block heteropolymer chains have a structure like (PMMA-*b*-PS-*b*-PMMA-*c*)_{*n*}, where ‘*c*’ denotes the linking agent, pentanediol. The structure can also be written as (PMMA-*b*-PS)_{*n*}, in which the PMMA block is twice longer than that in the initial triblock PMMA-*b*-PS-*b*-PMMA copolymer chain because each two PMMA blocks are connected together in the resultant multi-block copolymer.

Fig. 3 shows typical size exclusion chromatographs (SEC) of PMMA-*b*-PS-*b*-PMMA and multi-block copolymer (PMMA-*b*-PS)_{*n*}. Both peaks have a polydispersity index (M_w/M_n) ~ 1.25. The weight average molar mass of the resultant multi-block copolymer was 4.72×10^5 g mol⁻¹, indicating that on average, more than 20 triblock copolymer chains were coupled together. According to a normal definition of block copolymers, this is a 40–50-block copolymer. The results have been confirmed by static laser light scattering. For comparison, a control experiment was performed at 45 °C at which no self-assembly of the triblock PMMA-*b*-PS-*b*-PMMA chains was detected by LLS. We were not able to detect any long multi-block heteropolymer chain by SEC and LLS after a week, indicating that self-assembly is a key element for the preparation of long multi-block copolymers.

Similarly, (PI-*b*-PS-*b*-PI-*c*)_{*n*} was also prepared *via* the SAAP method using (CICOCO)[polyisoprene-*b*-polystyrene-*b*-polyisoprene](COCOCI) ((CICOCO)[PI-*b*-PS-*b*-PI](COCOCI) as starting material and pentanediol as linker in THF/hexane (1/4, v/v) at 25 °C. Fig. 4 shows that the formation of long multi-block copolymer chains in terms of the shift of the peak position of the hydrodynamic radius distribution $f(R_h)$ from ~ 4 nm to ~ 160 nm. The small peak reveals that the polymerization was incomplete.

In summary, using the self-assembly of block copolymer chains in a selective solvent or a solvent mixture to concentrate the reactive functional ends of polymer blocks and increase the coupling efficiency, we are able to chemically join each two ends of different polymer blocks together to form long multi-block chains. We are attempting to perfect the coupling efficiency of the process.

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Notes and references

[†] Preparation of (CICOCO)[PMMA-*b*-PS-*b*-PMMA](COCOCI): a 0.75 M lithium-biphenyl-THF solution (2.00 mL, 1.50 mmol)¹¹ was diluted with

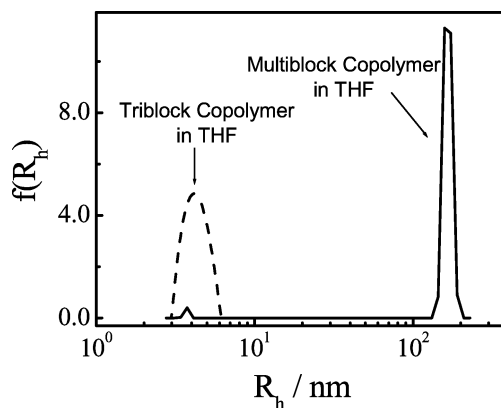


Fig. 4 Hydrodynamic radius distributions ($f(R_h)$) of individual triblock PI-*b*-PS-*b*-PI copolymer chains and multi-block (PI-*b*-PS-*b*-PI-*c*)_{*n*} copolymer chains in THF at room temperature, where the polymer concentrations are $\sim 1 \times 10^{-4}$ g mL⁻¹.

THF to 100 mL and cooled to -40 °C, to which was slowly added 0.5 mL of a THF solution of styrene (4.80 g in 20 mL of THF, 46.1 mmol) with stirring. The solution immediately changed from colorless to orange, and the mixture was stirred for 0.5 h at -40 °C. The remainder of the THF solution of styrene was then added, and the reaction mixture was stirred for another hour at -40 °C. To the resulting active polystyrene solution was quickly added a THF (10 mL) solution of methyl methacrylate (0.20 g, 2.00 mmol), and the solution changed from orange to light yellow. The reaction mixture was stirred for 2 h at -40 °C. To the resulting Li[PMMA-*b*-PS-*b*-PMMA]Li solution was added oxalyl chloride (3.00 g, 23.6 mmol). The solution was slowly warmed to room temperature and stirred overnight. The functionalized triblock copolymer (CICOCO)[PMMA-*b*-PS-*b*-PMMA](COCOCI) was isolated by precipitation in hexane, and purified by precipitation three times from THF into hexane, and dried *in vacuo* to give a white powder (4.6 g, 92%). ¹H NMR (300 MHz, TMS, CDCl₃): δ 7.05–6.58 (br, aryl H), 3.61 (s, OCH₃), 1.83–1.27 (br, main chain CH, CH₂ and CH₃). M_w of the PS and PMMA blocks from SEC were 2.10×10^4 and 8.75×10^2 , respectively. $M_w/M_n = 1.25$.

[‡] Preparation of (PMMA-*b*-PS)_{*n*}: a solution (100 mL) of (CICOCO)[PMMA-*b*-PS-*b*-PMMA](COCOCI) (2.00 g, 0.11 mmol) in a mixture of solvent (CH₃COOCH₃/CH₃CN = 10/1, v/v) was heated to 45 °C and stirred for 5 h until the triblock copolymer was completely dissolved. This solution was cooled to 29 °C, to which was slowly added a solution of (6 mL) 1,5-pentanediol (HO(CH₂)₅OH; 12.5 mg, 0.12 mmol) and pyridine (32.0 mg, 0.41 mmol) in a mixture of solvent (CH₃COOCH₃/CH₃CN = 10/1, v/v). The reaction mixture was then stirred for 4 days at 29 °C. During the course of this reaction, a white precipitate was formed. This solid was collected by filtration, purified by precipitation three times from THF into hexane, and dried *in vacuo* to give a white powder (0.20 g, 10% based on the triblock copolymer used). The unreacted triblock copolymer was recovered by precipitation into hexane (1.72 g, 86%). ¹H NMR (300 MHz, TMS, CDCl₃): δ 7.04–6.58 (br, aryl H), 4.60 (br, OCH₂), 3.60 (s, OCH₃), 1.94–1.26 (br, backbone CH, CH₂ and CH₃). SEC: $M_w = 4.72 \times 10^5$ g mol⁻¹; $M_w/M_n = 1.23$.

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