

Rapid Communication

NOVEL SYNTHESIS OF LONG MULTI-BLOCK HETEROPOLYMER CHAINS WITH AN ORDERED SEQUENCE AND CONTROLLABLE BLOCK LENGTHS*

Chi Wu**, Zuo-wei Xie, Guang-zhao Zhang and Guo-fu Zi

Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong, China

Abstract It had very long been a dream in polymer science to synthesize long multi-block polymer chains with an ordered chain sequence and controllable block lengths. Using ionic or living free radical polymerization or furnishing each end of polymer blocks with a reactive functional group, one can only prepare heteropolymer chains with few long blocks, such as diblock and triblock copolymers. The most plausible result so far was a pentablock copolymer. Recently, using a combination of polymer physics and synthetic chemistry, we have invented self-assembly assisted polycondensation (SAAP). This communication reports the results of using this novel method to connect 10–100 triblock polymer chains together to form long multi-block heteropolymer chains with an ordered sequence and controllable block lengths.

Keywords Multi-block copolymer, Self assembly, Self assembly assisted polypolymerization, Novel polymer synthesis

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 both bulk and solution^[1–9]. The advancement of synthetic methods, such as ionic polymerization and living free-radical polymerization, has made the synthesis of various kinds of narrowly distributed diblock AB and triblock ABA copolymers possible.

In theory, one could alternatively 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 ends are terminated. This is why success in this direction has been very limited. The most plausible result with a reasonable yield so far was the preparation of pentablock copolymers^[10, 11].

Alternatively, one could, in principle, prepare narrowly distributed polymer blocks with two reactive ends and then join them together to form long multi-block heteropolymer chains^[4]. However, such a reaction stops the chain length increases because the reactive end groups are wrapped and hidden inside the coiled polymer chains in solution and also because the end concentration is too low. The reaction practically stops as soon as a few polymer blocks are coupled together. Therefore, the key problem is how to organize and concentrate the chain ends so that they can be effectively coupled together to form long multi-block heteropolymer chains.

On the other hand, it is known in polymer physics that block copolymer chains in a selective solvent can self-assemble into different core-shell-like nanoparticles with the insoluble block as the core and the soluble block as the shell^[6, 12–14]. The self-assembly forces the chain ends to organize and concentrate on the periphery or in the center of the nanoparticle, depending on the copolymer structure and the solvent selectivity^[7, 8]. Recently, realizing such an organization and concentration of the chain ends can effectively increase their reaction efficiency, we have invented the self-assembly assisted polycondensation, or called as, the self-assembly assisted polypolymerization (SAAP). Note that we intentionally used “polypolymerization” instead of “polymerization” because in this method, polymer chains instead of small monomers are “polymerized” (chemically coupled

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** Corresponding author: Chi Wu (吴奇), E-mail: chiwu@cuhk.edu.hk

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together) into a long multi-block heteropolymer chain.

To demonstrate this novel SAAP method, we used the most common triblock copolymer, poly(methyl methacrylate)-*b*-polystyrene-*b*-poly(methyl methacrylate) (PMMA-*b*-PS-*b*-PMMA). The number averaged molar masses of the PS and PMMA blocks from GPC were 1.68×10^4 and 7.00×10^2 , respectively. The polydispersity index (M_w/M_n) is 1.25. The ends of the two PMMA blocks were terminated with reactive oxalyl chloride ($-\text{COCl}$). In a solvent mixture of methyl acetate and acetonitrile (10.0:1.0 in *V/V*), the copolymer is soluble at temperatures higher than 45°C , but self-assemble into a core-shell-like nano-structure with a collapsed PS core and a swollen PMMA shell at $\sim 29^\circ\text{C}$.

Figure 1 shows such a self-assembly in terms of the variation of the hydrodynamic radius distribution measured by laser light scattering (LLS). At high temperatures, there was only one peak located at 3–4 nm, representing individual triblock chains. The peak was split into two peaks at lower temperatures. The peak located at 30–40 nm indicates the self-assembly of the triblock copolymer chains, while the small peak remaining at 3–4 nm reveals that not all of the triblock copolymer chains were self-assembled as the nanoparticles. The self-assembly organized and concentrated the chain ends on the periphery so that we could couple each two ends of the copolymer triblock chains with a linker, pentanediol ($\text{HO}-(\text{CH}_2)_5-\text{OH}$), via condensation. The resultant long multi-block heteropolymer chains have a structure (PMMA-*b*-PS-*b*-PMMA-*c*)_{*n*}, where “*c*” represents the pentanediol linker.

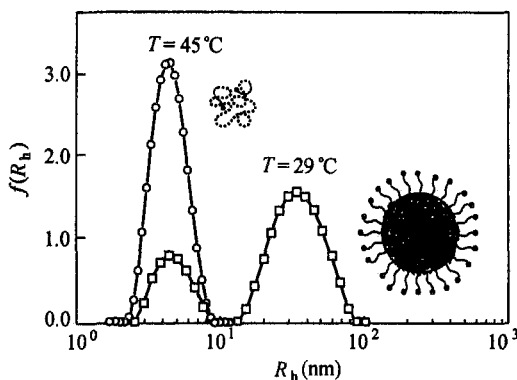


Fig. 1 Typical hydrodynamic radius distributions ($f(R_h)$) of individual triblock copolymer chains in a solvent mixture methyl acetate-acetonitrile (10:1 in *V/V*) at higher temperatures and the aggregates formed via the self-assembly of triblock copolymer chains at lower temperatures, where $f(R_h)$ s were determined by dynamic laser light scattering.

The high molar mass peak after the SAAP, as shown in Fig. 2, clearly shows that we have indeed successfully coupled copolymer triblocks together to form long multi-block (PMMA-*b*-PS-*b*-PMMA-*c*)_{*n*} chains. The NMR study has confirmed the chemical compositions of the triblock copolymer and the resultant multi-block copolymer. The weight average molar mass (M_w) and the polydispersity index (M_w/M_n) of the resultant long multi-block (PMMA-*b*-PS-*b*-PMMA-*c*)_{*n*} copolymer was 4.72×10^5 g/mol and 1.23, respectively. The high molecular weight tail in the distribution of (PMMA-*b*-PS-*b*-PMMA-*c*)_{*n*} reveals that hundreds of triblock copolymer chains were coupled together. To our knowledge, this is the first preparation of long multi-block copolymer chains with an ordered sequence and controllable block lengths.

It should be stated that we did a comparative study at a relatively higher temperature at which no self-assembly was detected by LLS. In principle, the condensation should be fast at a higher temperature, but we found that the reaction was practically stopped and we were not able to detect any long multi-block heteropolymer chain by GPC even after a very long reaction time. It convincingly showed that the assistance of the self-assembly is vitally important and critical in the polypolymerization of long copolymer blocks.

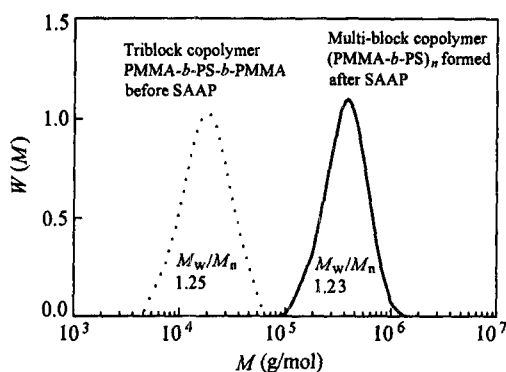


Fig. 2 Weight distributions of molar mass of triblock copolymer, PMMA-*b*-PS-*b*-PMMA, before self-assembly assisted polypolymerization (SAAP), and resultant long multi-block heteropolymer, (PS-*b*-PMMA)_{*n*}, after SAAP, where $W(M)$ s were determined by gel permeation chromatography (GPC).

It is worth noting that there exist a number of possible defects in the SAAP. The first kind of defect is the intrachain reaction, *i.e.*, the connection of the two ends from the same chain, resulting in a heteropolymer ring instead of a long linear chain. However, each chain end was surrounded by many chain ends from other chains so that the chance of forming a ring is small. The second kind of defect is the interparticle reaction; namely, the chain end on one nanoparticle reacts with the chain end on another nanoparticle, leading to much longer heteropolymer chains. The interparticle reaction can be suppressed if the polymer concentration is relatively low and the reactivity between the chain end and the linker is sufficiently high. This is because after the first end of the linker is reacted with a chain end on one nanoparticle, the second end of the linker should have a higher chance to react with one of the chain ends nearby on the same nanoparticle.

In summary, using triblock PMMA-*b*-PS-*b*-PMMA copolymer as a model system, we have demonstrated that the basic principle of the self-assembly assisted polypolymerization (SAAP) and successfully synthesized long multi-block (PMMA-*b*-PS-*b*-PMMA-*c*)_{*n*} copolymer chains. Note that the polymer blocks, the active chain ends and the linker used here can be easily varied to make other kinds of long multi-block copolymer or heteropolymer chains. It is foreseeable that with an optimal reaction condition, we could control the average number of triblock copolymer chains inside each aggregate to regulate the length of resultant multi-block heteropolymer chains. The optimization of the reaction condition and the application of this novel SAAP method to different block heteropolymers are under way.

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