

Multi-Polymerization: From Simple to Complex

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Abstract Multi-polymerization in which different polymerization mechanisms are performed together serves as an essential synthetic methodology for the construction of polymers with specific architectures, constitutions, and properties. Compared to single mechanism polymerization, the scope of multi-polymerization is significantly broadened by both the available synthetic methods and the synthesized polymeric materials. In this mini-review, multi-polymerizations are categorized into three major types based on the logical relationship between different mechanisms: sequential/tandem polymerization, orthogonal/concurrent polymerization, and hybrid polymerization. Each type of multi-polymerization is briefly introduced and summarized. This mini-review also discussed the importance of mutual influence in multi-polymerization and the potential research interests in this field.

Keywords Multi-polymerization; Sequential/tandem polymerization; Orthogonal/concurrent polymerization; Hybrid polymerization

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INTRODUCTION

The remarkable milestones of synthetic polymer chemistry in the past century are marked by the development of polymerization methods *via* a single mechanism, like condensation polymerization, radical polymerization, anionic/cationic polymerization, coordination polymerization, ring-opening polymerization, metathesis polymerization, *etc.*, as well as the related systems that simplify these methods to reduce unwanted side reactions to afford living/controlled polymerization. These polymerization methods and related systems constitute the bulk part of polymer chemistry and serve as the very basic foundation for the mass production of polymeric materials.

Despite its distinguished progress, polymer synthesis *via* a single mechanism is limited in several aspects, including the constitutions, architectures, and properties of the synthesized polymers. Therefore, multi-polymerization methods that utilize more than one polymerization mechanism are necessary to extend the scope of the polymerizations from a single mechanism. The use of multi-polymerization, however, could be quite complex, because a multi-polymerization system with two or more polymerization mechanisms may not proceed in the same manner as these mechanisms proceed themselves. This complexity actually originates from the fact

that different mechanisms could influence each other in different ways, including the monomer(s), solvent(s), initiator(s), catalyst(s), reaction condition(s), and so on. The influences between participating mechanisms for a multi-polymerization system could also take place during different stages of the reaction, like the initiation stage, propagation stage, and termination stage.

Challenged by the possible mutual influence between different polymerization mechanisms for multi-polymerization, three logical relationships and related polymerization methodologies are generally recognized (Fig. 1): (1) avoiding the mutual influence by performing the polymerization mechanisms separately in a certain sequence, known as sequential/tandem polymerization;^[1–13] (2) optimizing the multi-polymerization system by selecting polymerization mechanisms that have no mutual influence, known as orthogonal/concurrent polymerization;^[14–24] (3) dealing with the mutual influence directly by allowing different mechanisms performing together, known as hybrid polymerization.^[25–43] For a multi-polymerization with only two mechanisms (binary polymerization), the polymerization system could be directly described as sequential/tandem, orthogonal/concurrent, or hybrid. However, for a multi-polymerization with more than two mechanisms, the logical relationship between different mechanisms could be various combination of three basic logical relationships, and the corresponding polymerization system would be more complex, resulting in the high complexity of multi-polymerization. Considering the broad scope of multi-polymerization and large number of related publications, this review will give a brief summary to this field based on the three basic logical relationships.

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Invited Review

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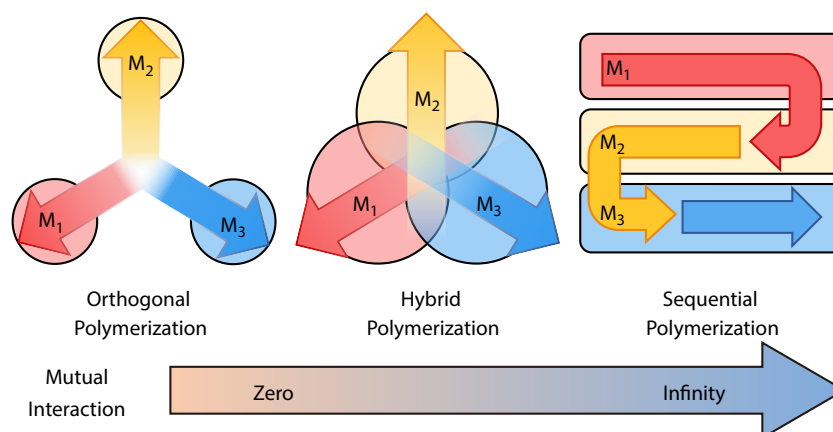


Fig. 1 Three basic logical relationships between different mechanisms for multi-polymerization judged by the extent of mutual interactions: orthogonal, hybrid and sequential.

THE SCOPE OF MULTI-POLYMERIZATION

Sequential/Tandem Polymerization

Of the three types of multi-polymerization, the most well-developed multi-polymerization method is sequential polymerization (also termed tandem polymerization) that different polymerization mechanisms take place in predetermined stages individually. During each stage of the polymerization, only one polymerization mechanism exists so that different mechanisms can have no mutual interference. One major advantage of sequential polymerization is the capability to combine different types of polymerization mechanisms. Because each mechanism will be terminated before the initiation of another, influences between participating mechanisms could be avoided. This flexibility of sequential polymerization makes it powerful for the synthesis of block copolymers and graft/bottlebrush polymers with different chain segments synthesized from different polymerization mechanisms. However, because sequential polymerizations with termination/purification for each step of the reaction is very close to a simple combination of single mechanism polymerization and could be quite costly for mass production, many reports on sequential polymerizations would indicate "one-pot" behavior that different mechanisms could take place continuously.

The sequential, one-pot multi-polymerization covers a wide range of mechanisms, including radical polymerization, coordination polymerization, cationic/anionic polymerization, ring-opening metathesis polymerization (ROMP), etc.,^[7,8,44–51] and reviews on this topic are available.^[52–57] Given the fact that different mechanisms need certain initiators, changing the reaction mechanism from the first mechanism to the second mechanism would require the presence of certain initiators, which could be provided either by the functional group of the existing polymers or the transformation of the existing chain terminals or functional group by additional reactions and/or reagents. For sequential polymerization that the second mechanism could be performed using the functional group of the first functional group, a typical strategy is to use a bifunctional initiator, monomer, or catalyst that could initiate two mechanisms at different conditions.^[7,9,46,48,58–62] As a typical example, bifunctional molecules with both hy-

droxyl group and alkyl bromide could be used for sequential polymerization of ring-opening polymerization (ROP) and atom transfer radical polymerization (ATRP).^[46,48] Using similar strategy, many different mechanisms, including ATRP, reversible addition-fragmentation chain transfer (RAFT) polymerization, ROP, ROMP, etc., could be combined into a sequential polymerization.

For sequential polymerization that the second mechanism requires the transformation of the existing chain terminals or functional groups, the transformation is usually performed elegantly and efficiently. For instance, Fors *et al.* reported a multi-polymerization method achieved by sequential cationic and radical polymerizations.^[63] As shown in Fig. 2, the chain terminal for cationic mechanism or radical mechanism could be switched to each other by the change of light wavelength. This allowed for the propagation via certain mechanism under selected wavelength to construct sequence-specified multi-block copolymers in one-pot. Similar strategy was widely used for the synthesis of copolymers with well-defined sequence using thermo-sensitive and electro-sensitive catalytic systems.^[63–65]

Orthogonal/Concurrent Polymerization

Different from sequential/tandem polymerization, orthogonal/concurrent polymerization enables the proceeding of different mechanisms simultaneously without mutual influence. This requires careful selection over the polymerization

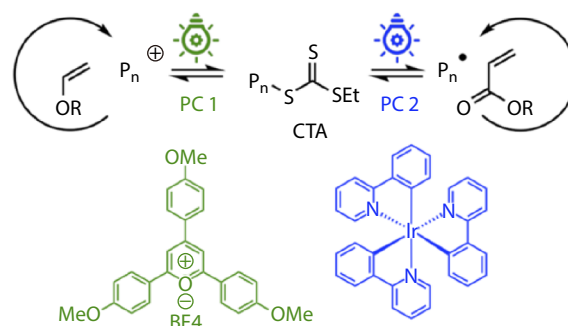


Fig. 2 Sequential polymerization of different olefin monomers at different wavelength. (Reproduced with permission from Ref. [63]; Copyright (2021) American Chemical Society).

to avoid potential interaction between mechanisms. The advantage of orthogonal polymerization is that different mechanisms could be performed together under a similar condition without the need of adding reagents or changing reaction conditions. One of the early reports on orthogonal polymerization described the orthogonal behavior of nitroxide mediated polymerization/ATRP and coordination ring-opening polymerization, as demonstrated in Fig. 3.^[66] Since the two mechanisms could be performed quite smoothly with the presence of each other, and the reaction conditions for both reactions are quite close, the combination of the two mechanisms was used for the synthesis of block copolymers and bottlebrush polymers. The authors also demonstrated that no new intermediate was observed to show that the mutual influence did not exist between the two mechanisms.

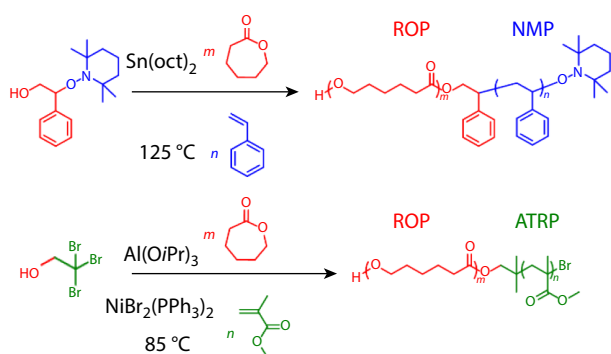


Fig. 3 Orthogonal polymerization of styrene/methyl methacrylate and caprolactone in one-pot. (Reproduced from Ref. [66]; Copyright (1998) John Wiley and Sons).

However, considering the fact that orthogonal polymerization requires that at least one mechanism is quite inert to other mechanisms and reagents, constructing an orthogonal polymerization method could be quite challenging. To avoid influences between participating mechanisms, many orthogonal polymerization methods include the use of "click" chemistry because of its high specificity and efficiency.^[19,67–69] For instance, a type of ABC triblock copolymer could be synthesized by the orthogonal polymerization using CuAAC "click" reaction and Diels-Alder reaction, as shown in Fig. 4.^[70] Since both the "click" reaction and the Diels-Alder reaction had high selectivity towards functional group, the two reactions had no relationship on mechanisms

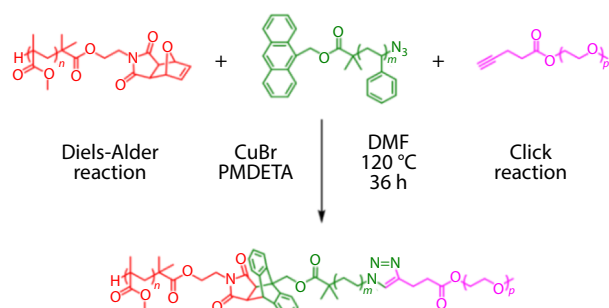


Fig. 4 Orthogonal polymerization of "click" reaction and Diels-Alder reaction. (Reproduced with permission from Ref. [70]; Copyright (2008) American Chemical Society).

and could be performed together to construct triblock copolymers.

Hybrid Polymerization

Compared to sequential polymerization and orthogonal polymerization, hybrid polymerization is a relatively new strategy for multi-polymerization. Different from orthogonal polymerization that only enables the combination of mechanisms without mutual influence, hybrid polymerization is more flexible that it allows for the combination of mechanisms with mutual influence. This affords hybrid polymerization a wide range of compatibility considering different mechanisms. For instance, our group proposed the hybrid polymerization of a substituted cyclooctene monomer that could be polymerized *via* both ring-opening metathesis mechanism and cross metathesis mechanism, as shown in Fig. 5.^[71] The two mechanisms could take place concurrently using the second or third generation Grubbs' catalyst. The hybrid behavior of the polymerization was confirmed by the study over the reaction kinetics. The kinetic behaviors of the hybrid polymerization were significantly different from the kinetic behaviors of each individual mechanisms, indicating the mutual influence between the two mechanisms. We further found that this mutual influence was temperature-dependent, which allowed for the control of the hybrid polymerization behavior. This strategy was used for the synthesis of linear and hyperbranched polyolefins with tuneable branching architecture and degree of branching (DB).^[71,72]

Later on, our group also reported the hybrid polymerization of two radical mechanisms: reversible complexation mediated polymerization (RCMP) and RAFT polymerization.^[73] By the hybridization of the two living radical polymerization techniques, we demonstrated that the RCMP method could be modified to afford better control over the polymerization behavior by the interaction between the two radical mechanisms (Fig. 6).

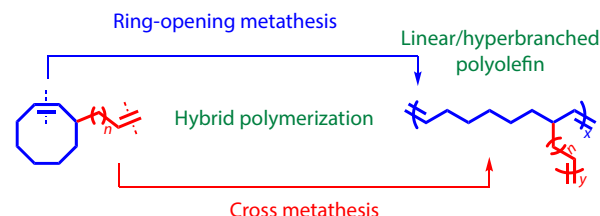


Fig. 5 Hybrid polymerization of substituted cyclooctenes *via* ring-opening metathesis and cross-metathesis. (Reproduced with permission from Ref. [71]; Copyright (2018) American Chemical Society).

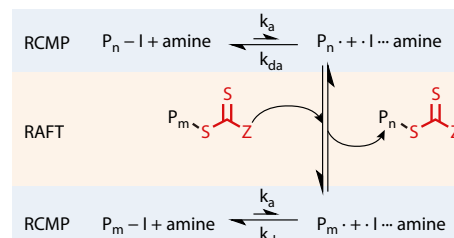


Fig. 6 Hybrid polymerization *via* RCMP and RAFT. (Reproduced with permission from Ref. [73]; Copyright (2020) American Chemical Society).

Many other research efforts on hybrid polymerization utilized different types of monomers with significant structural difference and reviews on this topic are available.^[26] Early researches could trace back to the 1960s for the hybrid copolymerization of vinyl monomers and cyclic monomers *via* cationic mechanism.^[40] For instance, the hybrid copolymerization of styrene and 1,3-dioxolane was reported in 1966 *via* cationic copolymerization,^[40] and the hybrid copolymerization of vinyl ethers and epoxides in 1983.^[34] Besides cationic mechanism, our group also described the anionic polymerization/copolymerization of glycidyl methacrylate (GMA) *via* vinyl polymerization and ring-opening polymerization (Fig. 7).^[27–33] The two mechanisms were performed in one-pot simultaneously and interacted with each other for the synthesis of hyperbranched polymers. Zhang *et al.* also reported the hybrid copolymerization of acrylates and lactones using *t*-BuP₄ as the catalyst, and the copolymerization behavior was observed, suggesting that the cyclic monomer and the vinyl monomer could be copolymerized successfully.^[39]

Besides the hybrid copolymerization *via* cationic/anionic polymerization mechanisms, some other mechanisms are also reported for hybrid copolymerization. As shown in Fig. 8, Hong *et al.* reported the hybrid copolymerization of acrylate monomers and cyclic thiirane monomers *via* RAFT mechanism and ROP mechanism.^[35] The resultant copolymers suggested that the two monomers could be polymerized together *via* two mechanisms, demonstrating the hybrid polymerization behavior.

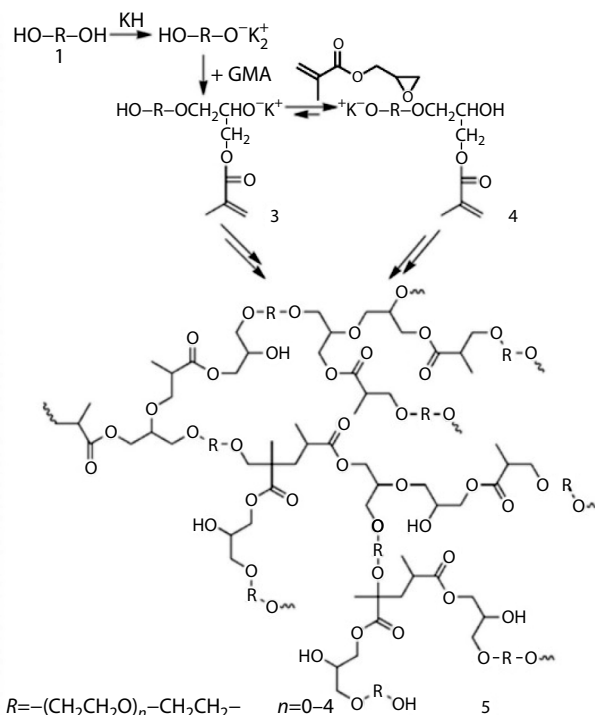


Fig. 7 Hybrid copolymerization of glycidyl methacrylate (GMA) *via* anionic mechanism. (Reprinted with permission from Ref. [27]; Copyright (2009) John Wiley and Sons).

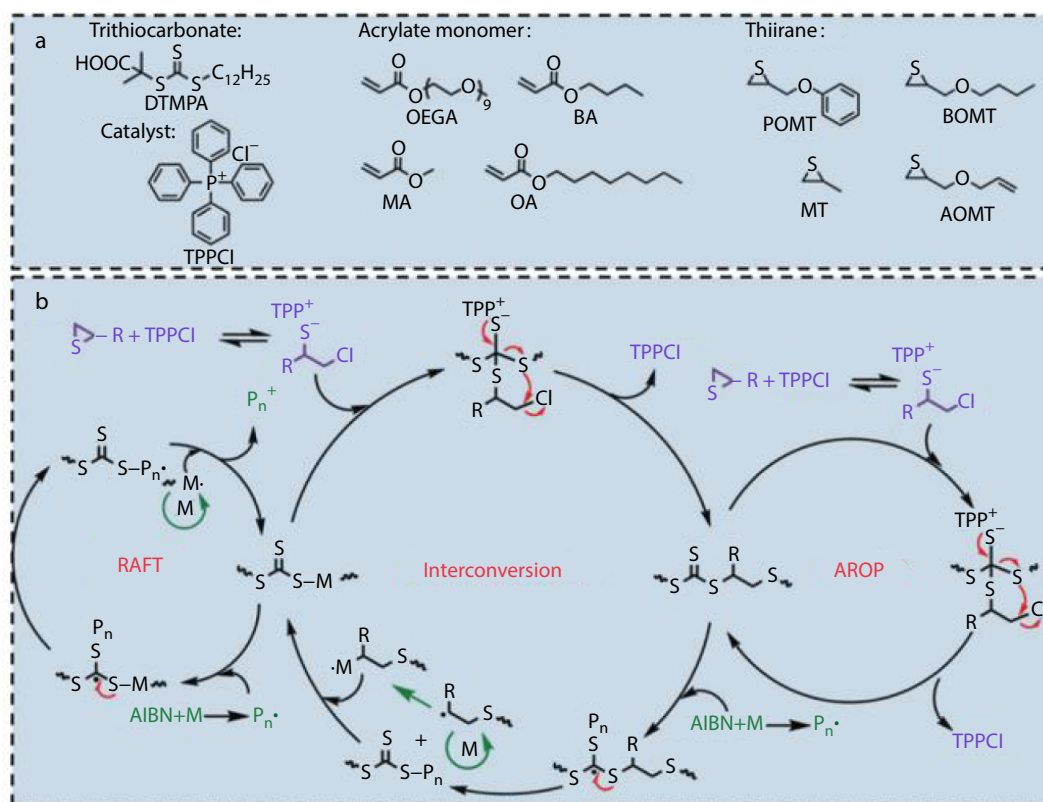


Fig. 8 Hybrid copolymerization of acrylate type monomer and thiirane type monomer *via* ROP and RAFT. (Reproduced with permission from Ref. [35]; Copyright (2022) The Royal Society of Chemistry).

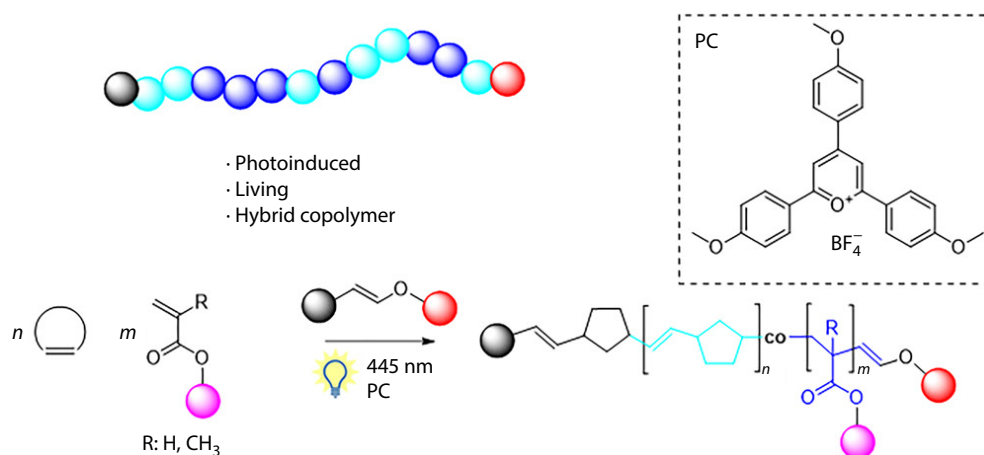


Fig. 9 Hybrid copolymerization of cyclic olefins and acrylates via ROMP and cationic radical polymerization. (Reproduced with permission from Ref. [25]; Copyright (2019) American Chemical Society).

Krappitz *et al.* reported the use of metal-free ROMP for the hybrid polymerization of norbornenes and acrylates *via* both ROMP and cationic radical mechanisms (Fig. 9).^[25] The two mechanisms could be realized using photo-sensitive catalysts that catalyzed both transformations. The synthesized polymers contained both poly(norbornene)s and poly(acrylate)s in their backbone and could be hardly obtained using other methods.

It is worth noting that the polymerization mechanism for some reported hybrid copolymerization systems did not vary much for different monomers, but the difference in the monomer structure would certainly bring mechanistic variation because of the difference in the structure of living center and the difference in the driven force of polymerization. However, since this part of research focused primarily on the structure of the synthesized polymer, the mutual influence between the polymerization mechanisms for each monomer was rarely mentioned, which could be very interesting indeed.

PERSPECTIVE

Multi-polymerization is a charming research area that enables the design of various types of polymers not accessible by single mechanism polymerization. However, the description over detailed multi-polymerization systems in different reference reports can be quite complex. Key words like "orthogonal", "concurrent", "sequential", "tandem", and "hybrid" are commonly used while their definitions are unclear and not uniform.^[15,16,26,74] One profound reason is that previous researches focused on the elegant design of these multi-polymerization systems to synthesize target polymers instead of discussing the logical relationship and mutual interaction between different mechanisms. Therefore, the influences between participating mechanisms remain unsolved for many multi-polymerization systems, restricting the controlled preparation of resulted polymers dramatically.

The reason for lacking of researches on influences between participating mechanisms is that the mutual interaction between/among different polymerizations can be hardly described, as we recently pointed out.^[75] With so many influen-

tial factors to consider for a multi-polymerization system, it is very challenging to afford a precise and comprehensive description over the influences between participating mechanisms.

To overcome this difficulty, our recent researches have suggested that it is possible to describe influences between participating mechanisms *via* the assessment of the reaction kinetics and thermodynamics.^[75] By comparing the kinetic/thermodynamic behaviors of each mechanism in a multi-polymerization system and the corresponding kinetic/thermodynamic behaviors of each mechanism under similar condition without the interference of other mechanism, the influences between participating mechanisms can be quantitatively calculated using the kinetic/thermodynamic model we proposed. We established a mathematical model that could be used to calculate the strength and related conditions of mutual interactions using a hybrid function.^[75] This allows us to study the mutual influence between mechanisms directly from the kinetic/thermodynamic behaviors of each mechanism. The calculated value of mutual influence can tell us whether or not the mutual influence exists between different mechanisms.

Using this theory, the relationship between hybrid polymerization and other multi-polymerization can be easily identified: the multi-polymerization with measurable influence between participating mechanisms belongs to hybrid polymerization; the multi-polymerization with infinite mutual influence between different mechanisms belongs to sequential/tandem polymerization; the multi-polymerization without any mutual influence between participating mechanisms belongs to orthogonal/concurrent polymerization. In fact, both sequential/tandem polymerization and orthogonal/concurrent polymerization are two boundary conditions for hybrid polymerization. For sequential/tandem polymerization, the infinite mutual influence between mechanisms indicates that the polymerization mechanisms have to be arranged in a specified sequence to avoid the mutual influence. This theory provides the basic foundation for the study on the relationship between different mechanisms of multi-polymerization, and can help design more attractive and valuable multi-polymerization systems by the combination of different kinds of single mechanism polymerization.

With progresses in both theory and method, it is reasonable to envision that multi-polymerization will play a more essential role in various fields of industrial applications. The use of multi-polymerization would enable the performing of different polymerization mechanisms simultaneously, therefore facilitating the construction of polymers or composites with different constitutions and structures originating from different polymerization mechanisms. Given the fact that polymer synthesis *via* multi-polymerization methods could be achieved in one-pot, it is both time- and energy-efficient and therefore attractive for mass productions.

BIOGRAPHIES

Ning Ren received his Ph.D. degree from Shanghai Jiao Tong University (SJTU) in 2019 and joined the School of Chemistry and Chemical Engineering at SJTU in 2022. Ning's research focuses on multi-polymerization methods and mechanisms.

Xin-Yuan Zhu received his B.Sc. and M.Sc. degrees at Donghua University and obtained his Ph.D. degree at Shanghai Jiao Tong University. He joined the BASF research laboratory at the Institut de Science et d'Ingénierie Supramoléculaires in Strasbourg as a post-doctoral researcher from 2003 to 2005. He became a Full Professor for Polymer Science and Engineering at Shanghai Jiao Tong University in 2005. He focuses his research interests on polymerization methodology and functional polymers.

NOTES

The authors declare no competing financial interest.

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