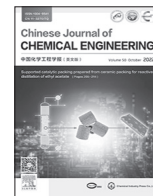




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Review

Progress of polymer reaction engineering: From process engineering to product engineering

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ABSTRACT

Polymer reaction engineering studies the design, operation, and optimization of reactors for industrial scale polymerization, based on the theory of polymerization kinetics and transfer processes (e.g., flow, heat and mass transfer). Although the foundation and development of this discipline are less than 80 years, the global production of polymers has exceeded 400 million tons per annum. It demonstrates that polymer reaction engineering is of vital importance to the polymer industry. Along with the maturity of production processes and market saturation for bulk polymers, emerging industries such as information technology, modern transportation, biomedicine, and new energy have continued to develop. As a result, the research objective for polymer reaction engineering has gradually shifted from maximizing the efficiency of the polymerization process to the precise regulation of high-end product-oriented macromolecules and their aggregation structures, i.e., from polymer process engineering to polymer product engineering. In this review, the frontiers of polymer reaction engineering are introduced, including the precise regulation of polymer chain structure, the control of primary aggregation structure, and the rational design of polymer products. We narrow down the topic to the polymerization reaction engineering of vinyl monomers. Moreover, the future prospects are provided for the field of polymer reaction engineering.

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1. Introduction

Since early 20th century, the development priority of the global chemical industry has gradually shifted from bulk chemicals to specialty chemicals. Although the production scale of bulk chemicals was expanding with the economic development, the profit margin was limited, and the product cost primarily depended on raw materials (e.g., crude oil). The rapid development in emerging industries (e.g., information techniques, modern transportation, biomedicine, new energy) creates a great demand for various specialty chemicals, which are typically high value and have relatively large profits that require a novel production technology. This caused a shift in the development of traditional chemical industry, from primary processing of resources to refined processing; from process optimization to products design innovation that fits the market demand, that in a nut shell, emphasizing precision in manufacturing and technology for products of specific performance or

function. Multinational chemical enterprises were therefore shifting core industries to adapt market and pursue high profits. Meanwhile, the academic entity put forward “Chemical Product Engineering” as a new direction of chemical engineering, the most representative of which was the report “Product engineering: the third paradigm of chemical engineering” made by James Wei of Princeton University [1]. Numerous important articles have since then been published, and the fundamental issues of chemical product engineering have been thoroughly investigated by worldwide scholars [2–9]. It is stated that chemical product engineering is a new branch of chemical engineering with the goal of designing, developing, and manufacturing specialty chemicals in a more scientific and efficient way, and the core content is the precise tailoring of chemical structures (Fig. 1) [10].

Polymer is a typical example for chemical products. In recent years, the market for bulk polymer has become saturated, while the demand for high-end polymer products keeps mounting. However, unlike small molecule products, the function/performance of polymer products derives from sophisticated structures, e.g., chain structure (or molecular structure), aggregation structure, multiphase/multi-component structure (Fig. 2) [11]. These differ-

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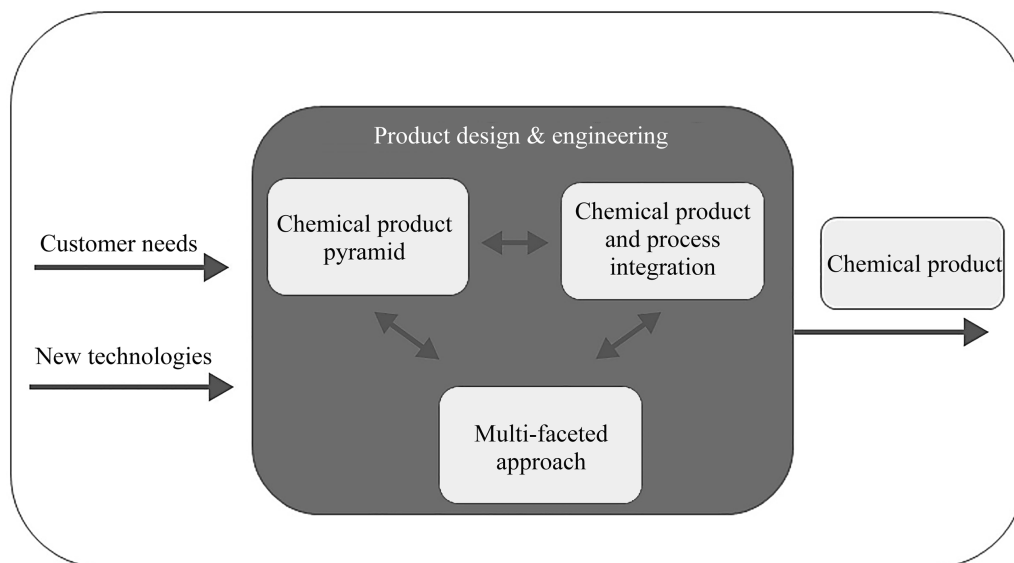


Fig. 1. Fundamental concepts of chemical product engineering. Reproduced from Ref. [10] with permission from Elsevier.

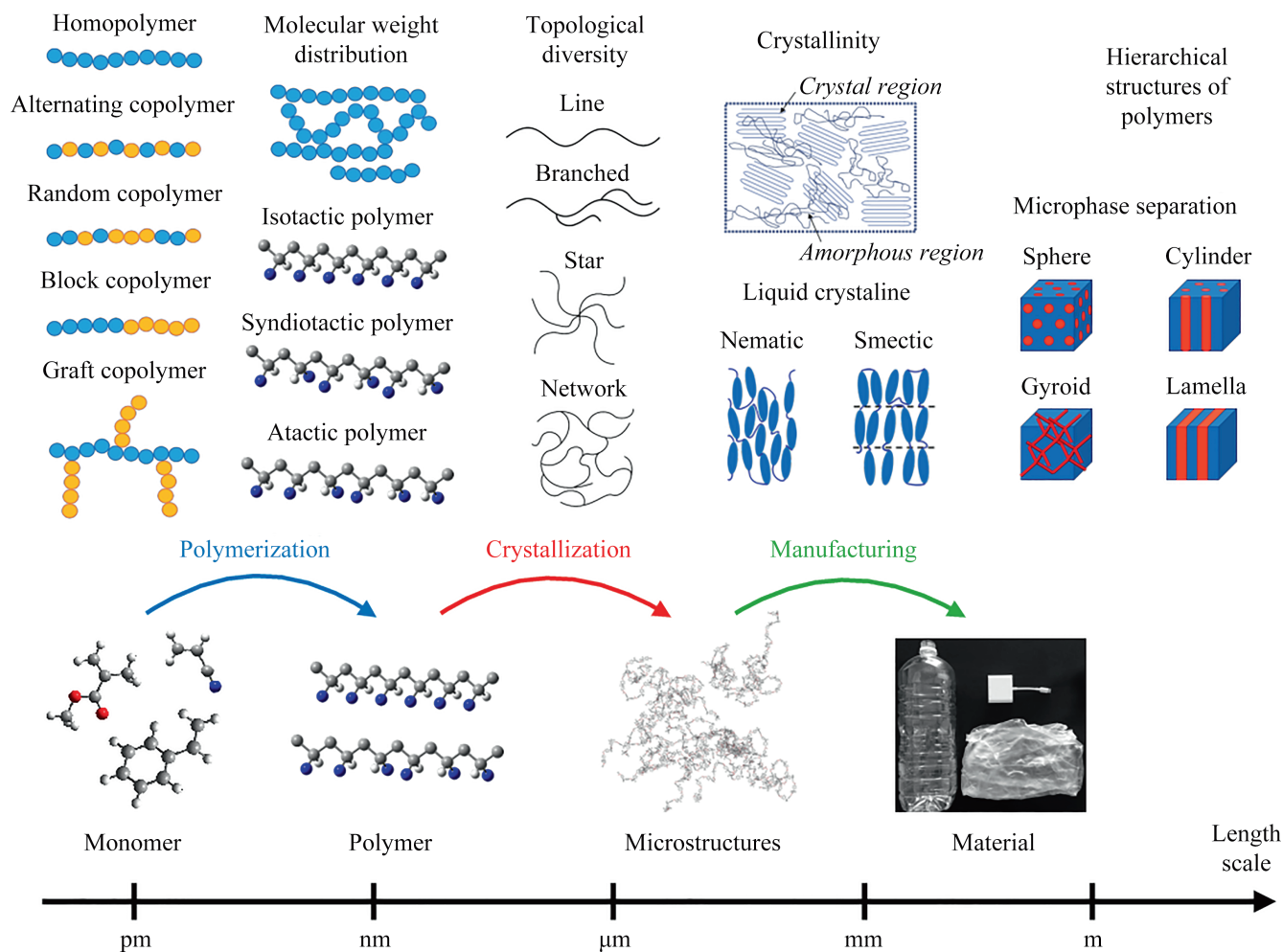


Fig. 2. The hierarchical structure of polymer products [11].

ent hierarchies are closely related to each other, and the lower orders could influence the higher ones, determining the performance and function of polymer products collaboratively. The

design and manufacture of high-end polymer products thus lie in the precise control of all-hierarchical structure, albeit it remains a great challenge.

The nano/micro-structure of polymer products depends on the production process [9], which is highly complex involving multiple polymerization mechanisms and reaction dynamics in viscous non-Newtonian fluids or suspensions/emulsions with a high solids content. The polymerization process covers from the molecular scale of polymeric monomers to the macro scale of the industrial production system, featuring distinct multi-scale characteristics. It not only produces a primary aggregation state utilizing monomer molecules to construct macromolecules with specific topological structures, but also tailors the aggregation structure by the macromolecules' interaction in an external field.

In the early stage of polymer reaction engineering, much attention was paid at flow, mixing, and heat/mass transfer of polymerization reactors and their effects on the reaction. Although polymer reaction engineering involves structural factors (e.g., morphology, molecular weight and its distribution), it mainly focuses on the energy-consumption of polymerization to achieve a low consumption, high efficiency, and stable process to develop targeted polymer products, thereby showing the distinct characteristics of polymerization process in this discipline. Nowadays, more and more researchers have noticed an increasing demand for high-performance and special-customized polymer products. They observed significant differences in performance/function between polymers synthesized with the same monomers but different chain/aggregation structures and gradually realized the limitations of achieving high performance of polymer materials just by post-processing. Herein, polymer reaction engineering gave out a new branch of precise design and tailoring of polymer structures based on the market demand and product performance/function, namely polymer product engineering (Fig. 3) [12].

On the one hand, polymer product engineering requires an in-depth research at micro-scale to precisely design chain/aggregation structure, and further achieving the controlled synthesis of polymer products. On the other hand, advanced sensing, big data, and artificial intelligence can be integrated into the process to achieve the rational design and manufacture of high-end polymer, thus tailoring the product according to specific performance/function requirement. This review will focus on the structure control and performance optimization of polymer products, reviewing and discussing chain/aggregation structure-related theories and methods, as well as the rational design and precise tailoring of polymer products in reverse. Because the rate and reaction heat of chain polymerization of vinyl monomers are much higher than that of stepwise polymerization of functional groups-containing

monomers, the focus of polymerization engineering research with kinetics as the core is mainly on the chain polymerization of vinyl monomers, and which will be the major topic of this review.

2. Precise Regulation of Polymer Chain Structure

Polymerization is a probabilistic event in which numbers of reactions occur simultaneously, leading to the polydispersity of molecular structures. The inconsistency of the residence time and the mixability in reactors affect polymer products, resulting in the wide distributions of molecular weights, and copolymerization composition/units. These differences in parameters define the aggregation state and the function of polymer products, which also explains the distinct performance of polymers, though they are prepared by the same monomers with a similar average molecular weight and comonomer content.

Szwarc *et al.* [14,15] demonstrated in 1956 that the living anionic polymerization was of great importance in regulating the chain structure of copolymer. Living polymerization makes it possible to design the molecular chain structure of polymer precisely and construct complex polymers (e.g., segmented/graft copolymer, star polymer, comb polymer and cyclic polymer). However, anionic polymerization is greatly limited by few applicable monomers and tough operating conditions. Since 1990 s, research in living free-radical polymerization [16] and living coordination polymerization [17] has been reported, the former of which includes nitroxide-mediated radical polymerization (NMP) [18], atom transfer radical polymerization (ATRP) [19], and reversible addition-fragmentation chain transfer polymerization (RAFT) (Fig. 4) [20,21]. These methods are widely applicable for polymerizations of most monomers with the easy operation. In living free-radical polymerization, the life span of the living chain prolongs to hours, running through the whole monomer conversion process, resulting in a more controllable and uniform molecular weight. Sufficient time for chain propagation thus makes possible the structure regulation of copolymer.

Polymer chemists have made great efforts to the regulation of chain structure in polymer products, including catalyst design and polymerization mechanism. However, even for the polymerization with the same parameters (i.e., raw materials, formula and polymerization mechanism), the obtained polymers can exhibit various chain structure owing to the differences in flow/concentration/temperature fields or the mixing degree in reactors. Characteristic polymer structures (e.g., multi-block, gradient, long-

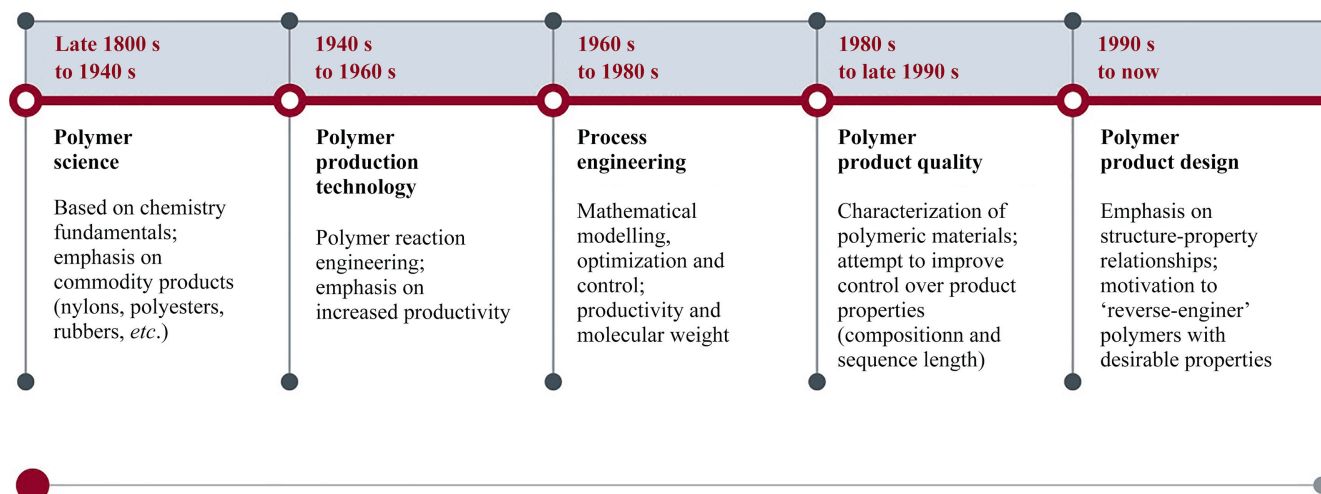
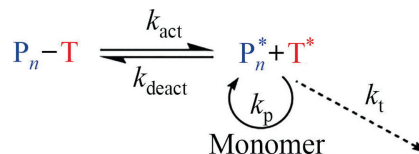


Fig. 3. Evolution of polymer science/engineering. Reproduced from Ref. [13] with permission from Wiley.

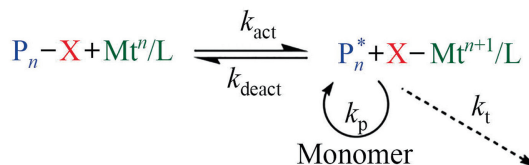
1) SFRP or NMP

Thermal dissociation of dormant species (k_{act}) provides a low concentration of radicals



2) ATRP

Transition metal activation (k_{act}) of a dormant species with a radically transferable atom



3) Degenerative transfer or RAFT

Majority of chains are dormant species that participate in transfer reactions (k_{exch}) with a low concentration of active radicals

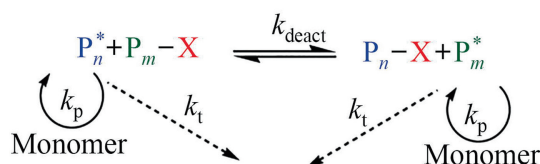


Fig. 4. The three main controlled/living radical methods. Reproduced from Ref. [21] with permission from Elsevier.

chain branching, bimodal distribution) with a high molecular weight yet a narrow distribution is difficult to be prepared via chemical methods, but hopefully through polymer reaction engineering.

For instance, Luo *et al.* [22] largely increased the concentration of free radicals and the polymerization rate while restrained the termination, taking advantage of the “isolation” effect of latex to free radicals in emulsion/mini-emulsion polymerization. Living emulsion/mini-emulsion polymerization was investigated using RAFT polymerization as model reaction, illuminating the “super-swelling” mechanism to the instability of polymerization system (Fig. 5) through thermodynamic simulation and experimental verification; by designing RAFT agents, emulsion/mini-emulsion polymerization realize controllable, fast and stable preparation of different polymer product, such as the copolymer of acrylic acid

and styrene with high molecular weight and narrow molecular weight distribution. The average radical number correlation formula in latex particle was also proposed to reveal the mechanism of the RAFT polymerization process and guide the improvement of polymerization rate [23–25].

Luo *et al.* [27,28] intensified the flow, mixing, heat/mass transfer performance in living free-radical polymerization by using external fields. They studied ATRP reaction in the external fields of light, electricity, ultrasound and microwave, proposing new methods of electrochemical regulated living free-radical polymerization and new mechanism of ultrasound-intensified polymerization, resulting in more efficient living polymerization.

According to the principle of polymer reaction engineering, batch or plug flow reactors are promising to prepare a narrow distribution of polymers by living copolymerization. However, the dif-

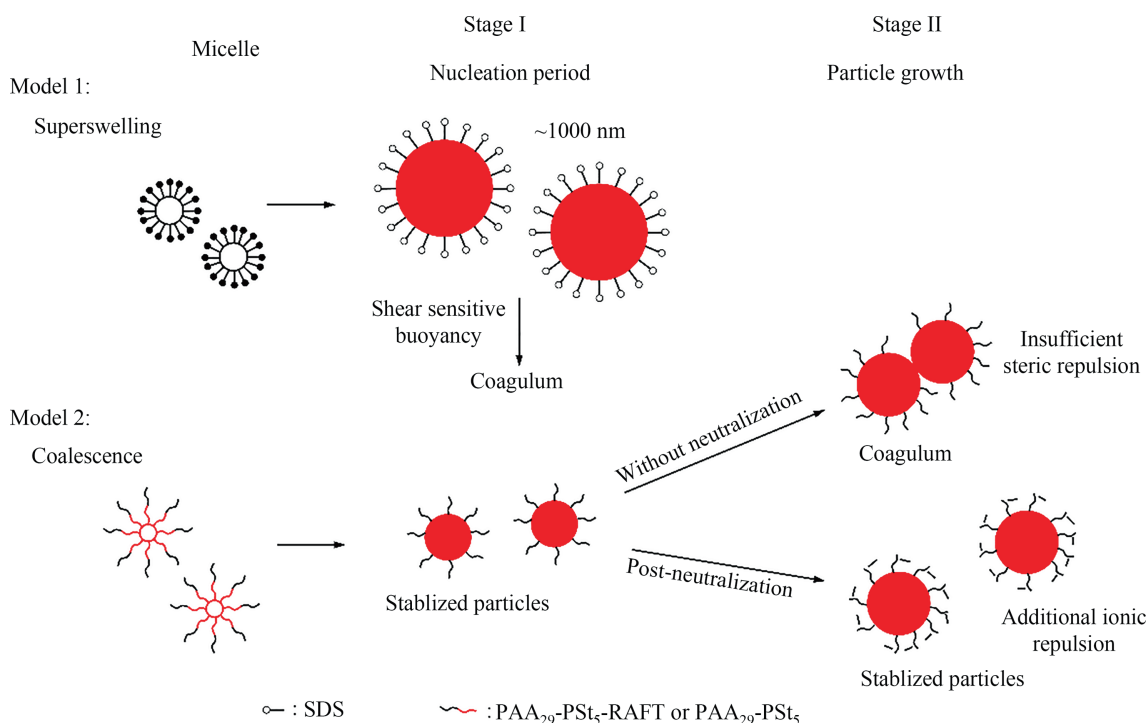


Fig. 5. Models for RAFT ab initio emulsion polymerization. Reproduced from Ref. [26] with permission from American Chemical Society.

ference in activity and reactivity rate of monomer lead to an uncontrollable gradient of copolymer units, where the beginning of chain is the homopolymer of active monomers, while the end is of inactive monomers. The heterogeneity of intermolecular structure is solved by living polymerization, but that of intramolecular still exists. Correspondingly, Yingwu Luo, Bo-Geng Li cooperated with Shiping Zhu of McMaster University [29,30], extended the research of traditional reaction kinetics concerning only the reactant concentration with time to all species of different chain structure (e.g., active chain, dormant chain and dead polymer chain) in living copolymerization process (Fig. 6). They set up and reduced the time-dependent differential equations of all species to finite element differential equations of 0–2 moments by moment method according to the polymerization mechanism. In the requirements of the molecular weight and distribution, composition and distribution of copolymer products, and the monomer distribution in copolymer chain, a specific semi-continuous monomer feeding policy was thus designed according to a semi-continuous reactor model for the precise tailoring of molecular structure, i.e., just by regulating the metering pump programmatically when feeding the monomers. For instance, researchers took homogeneous RAFT solution copolymerization of styrene and butyl acrylate as a model system, designed and customized a variety of copolymers with specific chain sequences, including uniform but disordered comonomer composition, forward or reverse linear gradients, hyperbolic tangent gradients, triblocks, etc. It provides an efficient approach to control molecular structures for developing new polymer materials [31–33].

On the grounds of above regulation technology of polymer chain structure that developed from polymerization reaction kinetics, Wang *et al.* [34–36] utilized a semi-continuous process for the RAFT solution copolymerization of acrylamide and diene monomer N,N'-methylenebisacrylamide (BisAM), customizing star and hyperbranched polyacrylamide (b-PAM) by changing the feeding method of BisAM (Fig. 7). The influences of the monomer molar ratio on the composition, polymerization rate, molecular weight

and distribution of the copolymer were investigated using the RAFT miniemulsion. They established a semi-continuous RAFT miniemulsion copolymerization model and a semi-continuous RAFT miniemulsion branched polymerization kinetic model by combining the semi-continuous reactor model. Styrene/butyl acrylate copolymers with uniform composition and linear gradient and hyperbranched polystyrene with uniform distribution of different branching densities were successfully customized by controlling the feed rate of comonomers, solving the difficulty in precise regulation of polymer branching density distribution [37,38].

The above polymers with tailor-made chain structure are advanced materials with good application prospects for their excellent properties. The triblock copolymer PS-*b*-PBA-*b*-PS is a new type of thermoplastic elastomer with tensile strength up to 10 MPa and elongation at break up to 500 % [24]; V-shaped gradient sequence copolymer St/BA, high molecular weight triblock copolymer polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) and polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS) have good shape memory properties [39]; and cationic polyacrylamide with complex sequences and topological structures as cross-linking and hyperbranching is ideal for water treatment, due to its good solubility and better flocculation performance [40].

Combining the polymer reaction engineering with olefin living coordination polymerization and cascade polymerization can promote the high performance of polyolefin materials. Bimodal molecular weight distributed polyethylene and two-block or three-block chain structured ethylene/1-octene copolymer were precisely customized using the new Fujita catalyst on the basis of reaction kinetics and the modeling of the polymerization process [41]. The interchain composition distribution of the resulting block polyolefins is much lower than that of commercial block copolymers prepared by chain shuttling polymerization, exhibiting superb reversible multi-shape memory properties. Based on the elementary reaction of ethylene tandem polymerization, a tandem polymerization model with ethylene as the only monomer can thus be established via a moment method combined with the mass

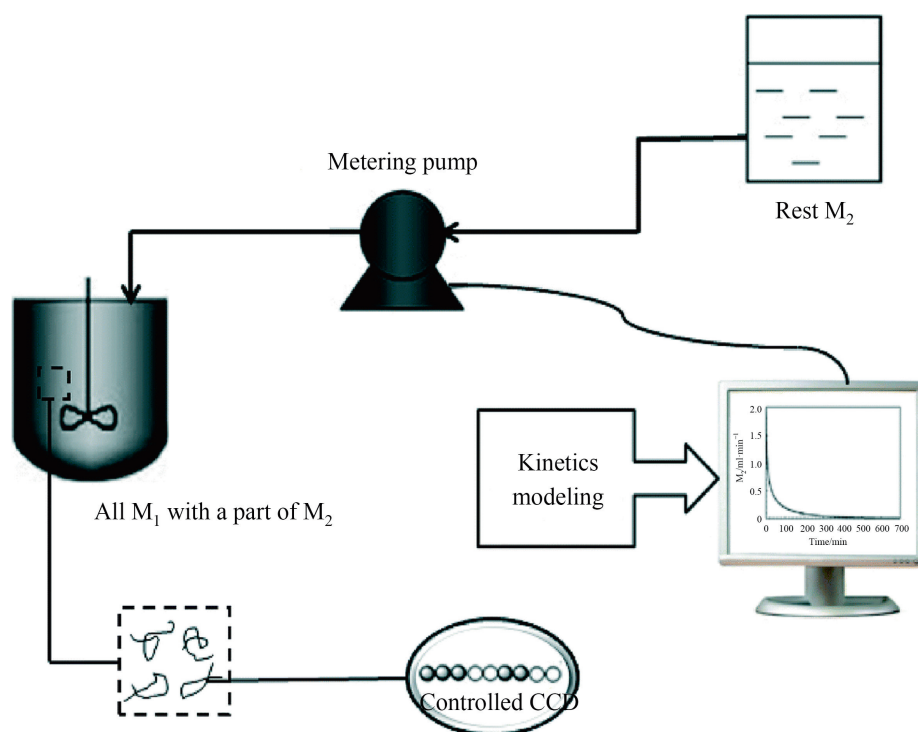


Fig. 6. Model-based monomer feeding policy. Reproduced from Ref. [29] with permission from Wiley.

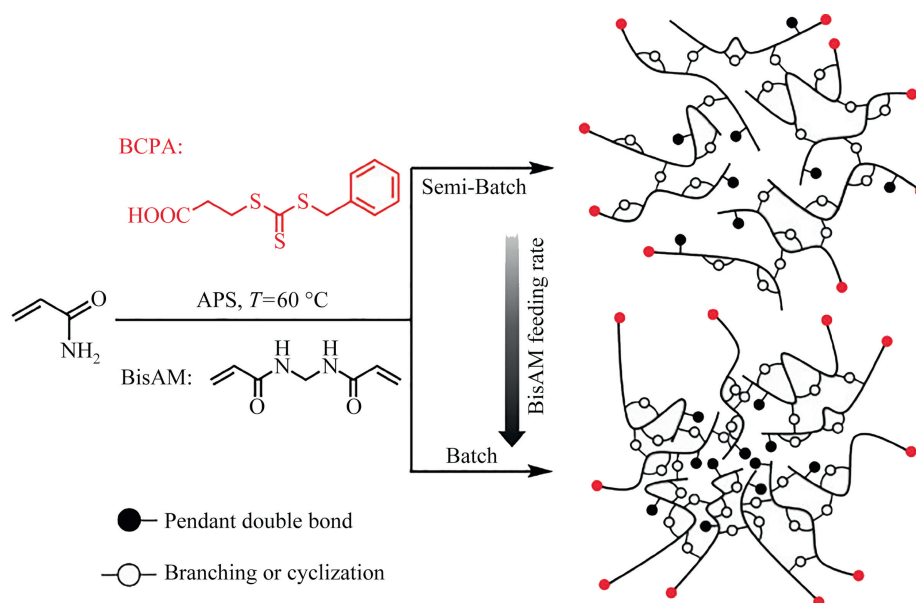


Fig. 7. Synthesis of hyperbranched polyacrylamide using batch or semi-batch polymerization. Reproduced from Ref. [35] with permission from American Chemical Society.

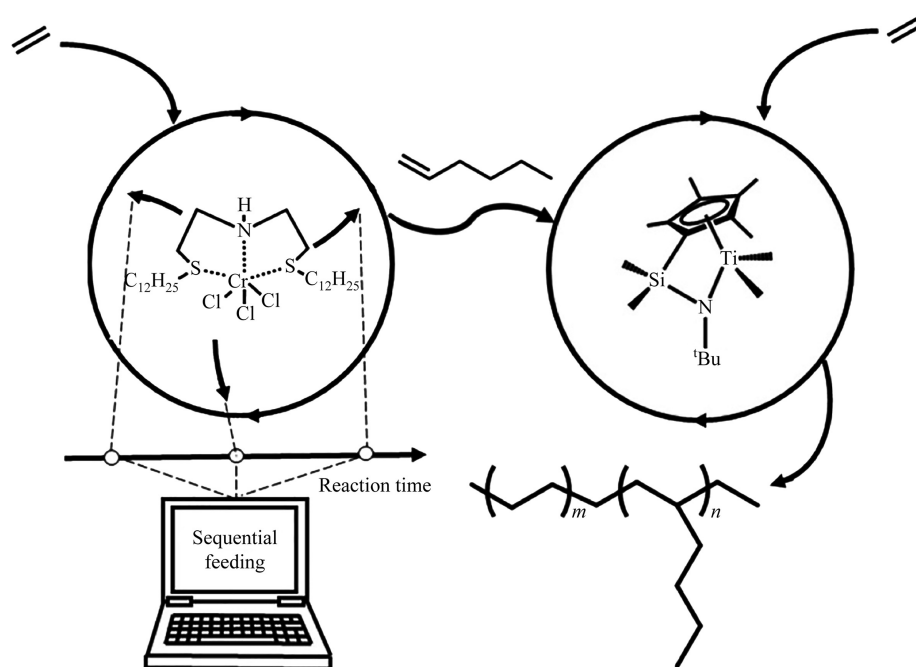


Fig. 8. Tailoring ethylene/1-hexene copolymers from ethylene stock with a model-guided catalyst feeding policy. Reproduced from Ref. [42] with permission from American Chemical Society.

balance of each species (Fig. 8). The catalyst feeding strategy was designed *via* model calculation, and the composition and distribution of ethylene/1-hexene copolymers were customized according to the requirements of targeted product composition, paving a new way for developing high-performance ethylene/ α -olefin copolymers [42].

Copolymers with the required structure can be precisely tailored by kinetic modeling and a programed semi-continuous monomer feeding strategy during living polymerization processes of vinyl monomers. This technology of regulating the chain structure numerically extends the manipulation of the molecular structure of polymer product to the distributions of molecular weights, copolymer compositions, chain sequences,

branching densities, and even cross-linking densities. Thus, even polymerization systems with the same monomer ratio can produce products with completely different molecular structures and properties. Polymer manufacturing technology, that utilizes the polymerization kinetic model to control the molecular structure programmably, is becoming a mature and effective method for the exploitation of high-end polymer products. Currently, this method is expanding into the industrial practice of multi-tank, loop, and multi-zone circulating fluidized bed and other polymerization reactors to achieve precise tailoring of complex chain structures and precise manufacturing of novel multi-block copolymers and gradient copolymers in continuous polymerization process.

3. Regulation of the Primary Aggregation Structure

Polymers, as an important class of chemical products, are the most complex chemicals in terms of structure [43]. The precise control of polymer aggregation structure is not only the key to realizing high-value polymer products, but also the core research content of chemical product engineering, which is the frontier of chemical engineering. Unlike small molecular products, the aggregation state of polymer form *in situ* during polymerization when monomers transform into macromolecules. Primary aggregation structure affects the polymerization process itself and subsequent polymer processing, as well as the properties of polymer products. Alloying technology in polyolefin reactors [44,45] and its derived multi-zone circulating fluidized bed technology (MZCR) [46,47] can manipulate the special primary aggregation structure of polymer products *via* changing the time/space monomer concentrations in polymerization. Especially, the MZCR technology that makes the homopolymer and copolymer structured with onion-like layer-layer coating, greatly improving the performance of polymer product.

Feng's group from Zhejiang University designed an atmosphere-switchable gas-phase polymerization device of stirred fluidized bed reactor [48,49]. The monomer atmosphere in reactor changes through the periodic pulse feeding of comonomer, and the high-impact polypropylene copolymer was successfully prepared with the particles remain relatively static. It has simplified the polymerization process that typically requires the cyclic switching of polymer growth particles in the two regions of circulation reactor. It shows that the switching frequency of gas significantly altered the structure of polymer product, thus affecting the mechanical properties. Luo *et al.* [50,51] took usage of the spatial confinement of emulsion oil/water interface of RAFT living miniemulsion polymerization to control the growth region and kinetics of the polymer chain, precisely tailoring the highly uniform polymer nanocapsules with controllable shell thickness [52,53]. It is promising to prepare materials with special aggregation structures by controlling polymerization using customized micro-nano (hollow) capsules as building blocks [54,55].

Wang *et al.* [56] designed macromolecular emulsifiers to riveted dimethylaminoethyl methacrylate (DMAEMA) segments on the surface of PMMA latex. The DMAEMA segment is protonated in CO₂, leading to a high hydrophilicity with dispersed latex particles,

while the DMEAME segment is deprotonated in N₂, which weakens the hydrophilicity and produces agglomerated particles. The introduction of stimuli-responsive polymers triggers the reversible dispersion and cohesion of aggregated particle assemblies, providing important implications for the development of the synthetic latex industry. Liu *et al.* [57–59] thoroughly investigated the assembly process of two-dimensional (2D) polymer materials such 2D covalent organic frameworks (Fig. 9). They precisely tailored the 2D polymer's micro-nano aggregation structure and its dispersed structure in matrix, inventing a series of bottom-up micro-nano manufacturing techniques, including reversible-polycondensation termination method, asymmetrical monomer exchange strategy and autoperforation nano-processing technique, *etc.* The precise tailoring of the multi-level structure of polymer products has been achieved to prepare a series of metastructured products controllably, broadening the applications of polymer products in the fields of micro/nano optical sensor and the catalytic olefin polymerization.

4. Conclusions and Outlooks

The ultimate goal of polymer product engineering is the rational design and precise tailoring of products. With a comprehensive understanding of product's structure–activity relationship, the controllable preparation for product structure with specific performance/function can be realized by apposite process engineering methods and processing techniques. The precise numerical control polymerization reaction engineering makes the research on specialty chemicals more scientific and rapid, thus meeting the market demand faster and better. Furthermore, the properties or functions of polymer products are very extensive and the structural levels related are extremely rich, which poses great challenges for research on the internal structure–activity relationship. Existing molecular simulation techniques and computational chemistry are far beyond the rational design of the most complex structured polymer. Therefore, one crucial challenge in realizing the precise tailoring of polymer products lies in the establishment of the structure–activity relationship model library.

In 2011, the United States took the lead in launching the Material Genome Initiative (MGI). They tried to establish precise property prediction models for some key materials though the building and sharing of databases and the application of cloud

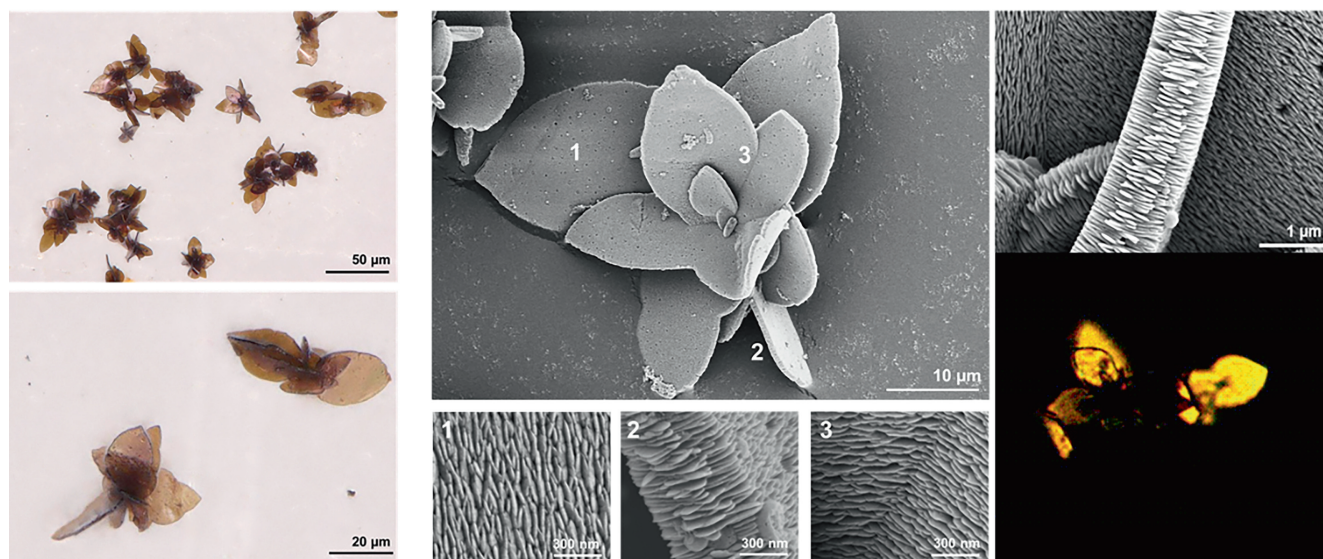


Fig. 9. Metastructured 2D polymers and their optical image under polarization. Reproduced from Ref. [60] with permission from American Chemical Society.

computing under the guidance of numerous experiments, shortening the research period and making up for the deficiencies of current molecular simulation techniques. It provides reference for the establishment of rational design for complex chemicals [61]. Additionally, high-throughput experimental techniques accelerate the screening of formulations and catalysts for chemical synthesis, and the characterization and analysis of product structure and properties. It serves as a huge driving force for explaining multi-level structure–activity relationship, and establishing model library and rational design of products, which has now become an essential method in polymer product engineering. Data mining and feature reconstruction that developed from big data techniques (e.g., machine learning and deep learning) with assistance of data sharing and high-throughput experimental technology, are anticipated to build up an accurate methods and models for artificial-intelligence-assisted prediction [62–64]. All these efforts will lead to an interdisciplinary research field—polymer informatics [11,65–68].

Numerical control manufacturing with the guidance of relevant predictive models is also a crucial methodology to precisely tailor the product structure. It is a quantitative control of the production process using computer programs. The current research hotspot – 3D printing technology, to a certain extent, has realized the numerical control manufacturing of the morphology and structure of polymer product at micron scale. Unfortunately, the majority of the 3D-printable materials nowadays are polymers or prepolymers with fixed molecular structure, limiting the regulation of polymer properties. Moreover, it requires investigations of polymerization reaction, curing, crystallization kinetics [62], and related guiding models, to precisely regulate the molecular/aggregation structure by 3D printing taking monomers as raw material.

Continuous expansion of reaction scale (i.e., from experimental synthesis to industrial application) inevitably leads to the significant “scaling effect”, causing inconsistent indicators for enlarged scale of chemical process. Precise scaling-up of chemical processes is the path to industrial safety and production quality. High-precision online detection of reaction process (e.g., acoustic/optical/electrical/magnetic techniques), as well as data mining and feature reconstruction methods derived from big data algorithm engineering, can be applied to develop reactor scaling-up theory with artificial intelligence. It performs as a transformative and intelligent platform for scale-up process. Specifically, computational fluid dynamics simulation and machine learning methods are employed to design and optimize macro/micro-reactor structures, matching the chemical reaction process with the characteristics of system flow and heat/mass transfer precisely. Furthermore, the processing and manufacturing of macro/micro-reactors are realized using traditional machining methods or combined with intelligent printing. A series of functional modules are integrated for unit operations (e.g., heating, cooling, reaction, separation). Ultimately, the characteristics of reactor flow fluid are monitored and feedback online by artificial intelligence algorithm, *in situ* analysis, and acoustic/electrical measurements. The quality, yield, selectivity and related indicators of product are examined as a function of operating conditions or module combinations. A database with detailed variable information can therefore be established to attain the precise regulation of scaling-up process and the optimization of operating condition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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