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Progress of Polymer Reaction Engineering Research in China

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In memory of Professor Zuren Pan, the pioneer of PRE in China

The polymer industry in China has developed rapidly over the past 30 years, which can be greatly attributed to the active R&D conducted by Chinese scholars in polymer reaction engineering (PRE) and their cultivation of high level talents. The research focus on PRE in China has shifted from the application development to both applied and fundamental research at present. The PRE researchers closely collaborate with the enterprises and the world leading scholars. The research objective has been evolved from optimizing efficiency of polymerization processes to precise control of the structures of polymer chains and primary aggregates. This essay summarizes the history, characteristics, and latest progresses of the PRE research in China, with emphasis on the research activities at Zhejiang University.

1. Introduction

The polymer industry, regardless of the production capacity or technology level, has been developing rapidly in China over the past three decades. In 2014, the production of five synthetic plastics products, namely polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), and ABS, reached 50.73 million tons in China. Combining this figure with the outputs of synthetic fiber at 40.44 million tons and synthetic rubber at 2.94 million tons, they account for 24.4, 66.2, and 20.7% of the global productions, respectively.[1] Compared to the production data in 2004,[2] the outputs of synthetic plastics, synthetic fiber, and synthetic rubber in China have been, respectively, increased by 125.9, 207.8, and 98.6% in the 10 years' time. In addition, the quality of products and the production technology have also undergone a huge improvement.

Almost all enterprises in polymer industry in China are owned either by the state or by Chinese private investors. The rapid expansion in production scale and the large progress in production technology can be attributed to the energetic R&D conducted by Chinese scientists and scholars in the field of polymer reaction engineering (PRE), as well as their continuous cultivation of high level talents. This paper introduces the PRE research in China from three aspects: the history of development, research characteristics, and latest progresses.

2. History of the Development

The polymer industry and the research on polymer engineering in China started in the 1950's. By 1958, a

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Bo-Geng Li graduated from Zhejiang University (ZJU), China with a chemical engineering bachelor degree in 1982 before master studies in thermodynamics under the guidance of Prof. Ziquan Zhu at ZJU and doctoral studies in polymer reaction engineering (PRE) under the supervision of Prof. Zuren Pan, the pioneer of PRE in China. He received master and doctoral degrees of engineering science in 1984 and 1987, respectively. Then Bo-Geng joined Department of Chemical Engineering (DCE) of ZJU as a faculty member, and was promoted as a full professor in 1994. He was a visiting fellow in DCE of Loughborough University in UK in 1991–1992, and a senior visiting scientist in DCE of MIT in 1998. Bo-Geng was awarded as a Cheung Kong Professor by the Ministry of Education of China, and received the National Science Fund for Distinguished Young Scholars in 2001. Bo-Geng was appointed as Head of DCE, Executive Dean of Material Science and Chemical Engineering, and Dean of Engineering of ZJU, respectively. Currently, he is director of State Key Laboratory of Chemical Engineering at ZJU.

Wen-Jun Wang received a chemical engineering bachelor degree at Zhejiang University (ZJU), China in 1986. In 1995, he finished his doctoral thesis in the field of polymer reaction engineering (PRE) with Profs. Zuren Pan and Bo-Geng Li right after master studies in heat transfer under the supervision of Prof. Peiyun Gu at ZJU. He undertook post-doctoral research in PRE under the guidance of Profs. Archie E. Hamielec and Shiping Zhu at McMaster University in Canada. Then he spent his career in R&D and management positions with Coveright Surfaces Canada Inc. and Nexwood Industries Ltd, Canada for several years. He returned to China to join Department of Chemical and Biological Engineering of ZJU as a faculty member in 2008. He was a recipient of Thousand Talents Program of Zhejiang Province. Currently, he is a full professor of ZJU and an adjunct professor of McMaster University. He also serves as Director for International Collaborations in College of Chemical and Biological Engineering of ZJU.

number of small polymer production enterprises had been established. At the same time, Zhejiang University (ZJU), Chengdu Institute of Technology (now merged to Sichuan University), South China Institute of Technology (presently known as South China University of Science and Technology), and East China Institute of Chemical Technology (now called University of East China University of Science and Technology, ECUST) successively set up polymer engineering majors such as plastics engineering or rubber engineering, offered related courses, and provided training for undergraduate students and a few postgraduate students. However, because of the weak economy, many polymer engineering research at the universities was restrained to focus in the field of polymer processing, which required less expenditure for meeting experimental requirements than those needed for other areas. However, the emerging and increased research activities on PRE in the world in 1960's attracted great attention from some Chinese scholars and scientists in chemical engineering, like Prof. Zuren Pan and Prof. Gan-Tang Chen at ZJU.

Prof. Zuren Pan was very interested in polymer chemistry and engineering fundamentals. He tirelessly assisted his colleagues in the Teaching and Research Group (TRG) of Plastics Engineering at ZJU, in which he was the founding director, in translating some research papers written by European and American scholars. In addition, he also organized and launched research on free radical polymerization. In 1965, they published a representative paper titled "Composition Control on Vinyl Chloride/Vinyl Acetate Copolymers."[3] Pan and his co-workers in the TRG put forth great efforts to address fundamental questions from application and development, and also to conduct related experimental and theoretical studies. For example, they carried out research on suspension polymerization of vinyl chloride (VCM), studied the initiator decomposition kinetics, polymerization reaction kinetics, heat transfer and temperature control in reactors for the effective control on polymerization rate, degree of polymerization, and copolymer compositions, etc. At the same time, they also investigated the nucleation mechanism of polymer particles and influence of dispersant and agitation on the liquid–liquid dispersion characteristics, in order to have a better control on particle morphology of polymer products.[4] Based on these research works, Pan et al. published two monographs, namely "Free Radical Polymerization"[5] and "Suspension Polymerization,"[6] and a textbook entitled "Polymer Chemistry."[7] The textbook has been published with five editions so far and printed approximately 20 million copies over the past three decades. It has been widely used by undergraduate and graduate students majoring in chemical engineering, chemistry, and material sciences in Chinese universities.

Prof. Gan-Tang Chen was an expert in chemical reaction engineering with exceptional mathematical skills. He was also very interested in the polymerization kinetics and process modeling. In 1962, he presented his work of "Process Design on Ionic Solution Polymerization Operation" in the 4th national polymer symposium, and published it in the Chinese journal of *Polymer Communication* in 1964.[8] However, due to the "Cultural Revolution" occurred soon after, Chen experienced difficulty in carrying out his research work any further, as also suffered by most Chinese scholars during the 10 disastrous years. Not until after the end of "Cultural Revolution" in 1977 that Chen finally completed his work on the modeling of ionic solution polymerization and published the results in some domestic and international journals.[9,10] Thereafter, Chen published his "Notes of Polymer Reaction Engineering"[11] in the Chinese journal of *Progress in Chemical Engineering* in five

Figure 1. Professor Zuren Pan (1926–2012), the Pioneer of PRE in China.

consecutive issues, in which the PRE was systematically introduced to Chinese readers. On top of that, he published a book entitled "Fundamentals on Polymer Reaction Engineering" in 1991.[12]

Prof. Zuren Pan (Figure 1) was not only an excellent scientist, but also an outstanding leader. He founded the TRG of Plastics Engineering at ZJU in 1958. The name of the TRG was changed to Polymer Chemical Engineering in 1972. In 1990, it was further expanded and renamed as the Institute of Polymer Science and Engineering. Pan was the director of the TRG/Institute for three decades until 1992. Particularly in 1987, on behalf of the TRG of Polymer Chemical Engineering at ZJU, Pan coordinated the research groups of extraction separation from Tsinghua University, distillation separation from Tianjin University, and chemical reaction engineering from East China Institute of Chemical Technology and applied for the establishment of State Key Lab of Chemical Engineering (SKLoChE) in China. The proposal of SKLoChE was approved and funded with its research focus for the key lab at ZJU defined as PRE. The name of the lab at ZJU was given as SKLoChE Zhejiang University Polymer Reaction Engineering Lab (ZJU-PREL). At the same time, Pan also established world-wide collaborations with Prof. A. E. Hamielec's group at McMaster University in Canada, Prof. W. H Ray's group at University of Wisconsin-Madison in the United States, Prof. K.-H. Reichert's group at Technical University of Berlin in Germany, and some other world leading PRE research institutions or groups. These collaborations involved co-supervising doctoral graduate students and recommending his students who had become his colleagues to visit and conduct research overseas. The purpose was to continuously enhance the PRE research level at ZJU, to establish its international reputation, and to minimize negative effects of the "academic inbreeding" on research creativity. It should be noted that it was a common practice among Chinese universities to recruit their own graduates for faculty positions then, and this practice continued until very recently when the Chinese governments at different levels strategically and actively introduced various programs to attract overseas talents. Some of Pan's students have become outstanding researchers or enterprise leaders on PRE, for example, Prof. Xiulin Zhu, the President of Suzhou University; Prof. Qinmin Pan in Suzhou University; Prof. Shiping Zhu, Distinguished University Professor and Canada Research Chair in McMaster University; Profs. Zhixue Weng, Bo-Geng Li, Yingwu Luo, Wen-Jun Wang, Lianfang Feng in Zhejiang University; Dr. Tuyu Xie in DuPont Canada, and Dr. Jianfeng (Jeff) Lou in BASF (China) Corporation.

Under the leadership of Pan and his successors, by the end of the last century, the research activities on PRE at ZJU were mainly focused on two fields, namely polymerization kinetics and modeling and transport laws in polymer reaction systems.[13,14] The study on polymerization kinetics and modeling was not only aimed at homogeneous polymerization systems having high viscosities, but also at heterogeneous suspension polymerization, precipitation polymerization, emulsion polymerization, etc. The study on transport laws of polymer reaction systems included the rheology, mixing, diffusion, and heat transfer characteristics in homogeneous systems with high viscosities and in heterogeneous systems. Prof. Kai Wang, who was the first successor to Pan, made significant contributions to the field of transport laws in polymer reaction systems. He systematically studied mixing, power, and heat transfer characteristics in various stirred-tank reactors having different types of agitation. He established a series of correlations of these characteristic parameters with reactor structure parameters and fluid physical properties by using the method of dimensionless analysis, as required for reactor design and scale-up.[15,16] Starting from the 1st issue of volume 8 in 1985, a total of 14 seminar notes on "Polymer Reaction Engineering" written by Professors Zuren Pan, Huigen Yuan, Kai Wang, Zhixue Weng, et al. were consecutively published in the Chinese journal of *Synthetic Rubber Industry*.[17]

With the development of economy, the Chinese governments and enterprises have continuously increased financial supports for scientific R&D since the beginning of this century. The ZJU-PREL took the great opportunity to add new experimental reactors and instruments, as well as simulation softwares. The field of polymerization kinetics and modeling has been extended not only toward the controlled/living radical polymerization (CLRP) and olefin coordination polymerization, but also to the control of copolymer composition and distribution, copolymer sequence distribution, primary aggregate and other complex chain structures, and polymer morphology on top of the control of polymerization rate, polymer molecular weight, and molecular weight distribution (MWD).[18] The studies on transport laws in polymer reaction systems have also been expanded to extrusion reactor and fluidized bed reactor areas. Highly efficient computational fluid dynamics (CFD) method has been introduced to the transfer studies in polymer reaction systems.

In addition to ZJU, other scholars like Prof. Zhilian Tang from East China Institute of Textile Science and Technology (now known as Donghua University), and Prof. Gance Dai from ECUST have also carried out research on PRE in 1980's and 1990's. Tang was appointed as a guest researcher at ZJU-PREL. His research mainly focused on the polymerization process of Nylon 6. Dai's research concentrated on diffusion and rheology in the post-polycondensation process of polyesters and polymer processing. He published a book entitled "Transport Phenomenon in Polymer Processing."[19]

In the recent years, the Chinese scholars and scientists from institutes other than ZJU, who are active in the field of PRE, include Prof. Ling Zhao from ECUST, Prof. Zhenghong Luo from Shanghai Jiaotong University, and many others. Zhao joined the research on the post-polycondensation process of polyesters, which was led by Prof. Dai at the early stage. She is now focusing on polymer processing and modification with the aid of supercritical gas.[20] Luo received his Ph. D. degree from ZJU, and is currently working on modeling, simulation, and optimization of polymerization processes and polymerization reactors.[21,22]

China Petrochemical Corporation (SINOPEC) is the largest petrochemical enterprise in China, ranked the second in Fortune 500 in 2015. The corporation was established in 1983, through merging many small and medium-sized petrochemical companies owned by the former Ministry of Chinese Petroleum Industry. Its polymer production sector comprises not only the wholly owned and equity-holding subsidiaries, such as SINOPEC Beijing Yanshan Company Ltd. (Yanshan), SINOPEC Qilu Petrochemical Company Ltd. (Qilu), SINOPEC Yangzi Petrochemical Company Ltd. (Yanzi), SINOPEC Shanghai Petrochemical Company Ltd., and SINOPEC Guangzhou Branch, etc., but also the joint ventures with BP and BASF, such as Shanghai SECCO Petrochemical Company Ltd. and Nanjing BASF-YPC Company Ltd. SINOPEC also founded its research institutions, namely, Beijing Research Institute of Chemical Industries (BRICI) and Shanghai Research Institute of Petrochemical Technology (SRIPT) for R&D in the areas of polymerization catalysis, polymerization technology, and modification of polymer materials. BRICI, one of the earliest comprehensive petrochemical technology research institute founded in 1958, was integrated into SINOPEC in 1998. BRICI has been working on olefin polymerization and catalyst development from very beginning. Profs. Shipei Tang and Bingquan Mao and their co-workers made great efforts in developing a Complex II catalyst, which has been widely used in polypropylene production through the bulk polymerization of propylene from the refinery gas since 1980.[23–25] Thereafter, Mao and co-workers[26,27] further developed the N-type and DQ spherical catalysts. With a large specific surface area and excellent spherical morphology, the N-type catalyst possesses high activity and good stereoregularity and produces polymers with narrow MWD. The technology has been patented in China, Europe, USA, and Japan. Some US companies have paid royalties for the technology. The catalyst is recognized as one of most popular catalysts for polypropylene production worldwide, including Europe and America.[23] As a fourth generation catalyst for olefin polymerization, the DQ spherical catalyst can be used in the production of spherical polyolefin resins of high bulk density, and also the in situ synthesis of polyolefinic alloy together with reactor granule technology.[27,28] At the same time, Dr. Yu and co-workers. collaborated with several universities and enterprises working on the development of olefin polymerization technology.[28–30] Recently, Drs. Wen-Jun Wang and Bo-Geng Li of SKLoChE-ZJU collaborated with Yu for the development of polyolefinic elastomers. A production technology with continuous solution copolymerization of ethylene and α-olefin in a high-temperature high-pressure CSTR system catalyzed by a propriety single-site catalyst of BRICI has been developed. Moreover, SINOPEC has also established and sponsored a joint institute, UNILAB Research Center for Chemical Reaction Engineering, in 1983 with ZJU and ECUST for chemical reaction engineering R&D, including polymerization processes and reactors, to meet their demand in technology.

In 2010, SINOPEC reorganized its research institutes. The institutes in Yanshan, Qilu, and Yangtze subsidiaries were incorporated into BRICI and became its branch institutes. Among them, Qilu and Yangtze mainly focus on the development of polymerization technology and new resin products, while Yanshan concentrates on rubber. On the other hand, SRIPT pays much attention to catalysis and reaction technology of organic and fine chemicals. SRIPT also established several polymer research groups and branch institutes in SINOPEC Yizheng Chemical Fibre Company Ltd., SINOPEC Baling Branch, and SINOPEC Sichuan Vinylon Works Group for the development of catalysts, polymerization technologies, and new synthetic fiber products.

China National Petroleum Corporation (CNPC) is the largest oil and natural gas producer and supplier in China and the second largest polymer producers in China. The corporation was ranked as the fourth in Fortune 500 in 2015. The R&D activities on polymer engineering and technology in CNPC are mainly conducted by its own institute and its subordinate institutes in CNPC Lanzhou Petrochemical Company Ltd., CNPC Daqing Petrochemical Company Ltd., and CNPC Jilin Chemical Industrial Works Group, covering olefin oligomerization, polymerization catalysis, polymerization technologies, and new synthetic rubber products. Meanwhile, global leading enterprises, such as BASF, Dow Chemicals, and Dupont set up their R&D centers in China in the start of 21st century. More and more Chinese doctoral and master's graduates are recruited by these enterprises and become the main force for the development of polymerization technologies and polymer products.

3. Research Characteristics

Prior to the reform and opening of China in 1978, the Chinese government stressed on self-dependence and tight connection between scientific research and production practice. Therefore, the polymer production technology in China was almost exclusively self-developed at that time. Although, the PRE research was mainly conducted in universities, the activities focused on the application development. The aforementioned study on PRE of VCM at ZJU was a typical example. In that period, very few academic papers related to the research were published, but the cooperation with enterprises was very active. The research results were successfully transferred and applied to assist the development of various kinds of products and the design and scale-up of polymerization reactors for over 20 domestic PVC production enterprises, which made PVC a major polymer product in China that was completely self-developed. It created huge revenues for the enterprises.[4] The PVC technology received numerous national science and technology progress awards.

Polybutadiene rubber (PBR) was another major polymer product completely self-developed in China. In light of a wide range of subject areas involved in the polymerization process of PBR, the Chinese government organized a joint program called "Assembly Battle." In this arrangement, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (CIAC-CAS) was assigned to focus on the development of catalyst systems and polymerization technology, and enterprises on the production technology of butadiene (BD) and PBR products. Because of its research strength on PRE, ZJU was assigned to participate in the heat transfer enhancement in polymerization reactors, and also made outstanding contributions. Prof. Zhiquan Shen of CIAC-CAS made important contributions to the development of PBR, prior to joining ZJU in 1980. Shen and coworkers developed nickel and rare earth catalysts,[31–33] which laid the foundation for independent development of nickel and rare earth based PBR products in China.

In China, the universities are the major R&D forces. Even today, 30 years after the reform and opening, the Chinese enterprises are still lacking the ability to self-develop technologies. This is particularly true with small and medium private companies. The Chinese universities are still undertaking a large number of technology development projects entrusted by the enterprises. Figure 2 shows the research funding structure of the State Key Lab of Chemical Engineering (Zhejiang University) (SKLoChE-ZJU, which was renamed from ZJU-PREL in 2004) over the past 15 years. It can be seen that the research funding supported by the enterprises always accounted for over 60% of the total research money. Even with a fixed number of 20 full-time researchers at SKLoChE-ZJU, the research funding increased at an average annual rate of 12.6% from 1999 to 2013. On top of PVC and PBR, other technologies developed by SKLoChE-ZJU and its collaborated enterprises included the precipitation polymerization of acrylonitrile in aqueous medium for acrylic fiber manufacture using a "two-step" technique, scaling-up for specific carbon-fiber used polyacrylonitrile production reactor, suspension polymerization of styrene (St) for expanded polystyrene

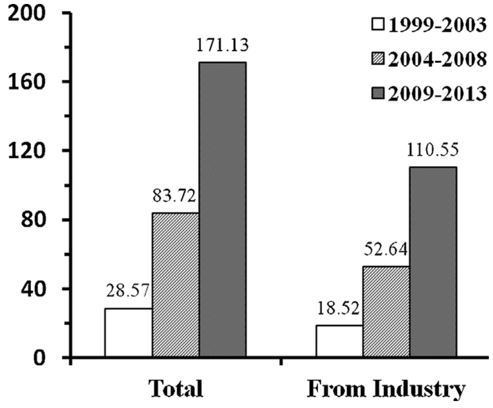

Figure 2. Research funding at SKLoChE-ZJU from 1999 to 2013.

(EPS) manufacture with a "one-step" approach, polymerization processes for high-impact St-containing resins including AAS, ACS, and MBS, random bulk copolymerization of St and maleic anhydride, emulsion copolymerization of St and BD, anionic solution copolymerization of St and BD, design and scaling-up of specific reactor for painting and coating, dispersion polymerization of tetrafluoroethylene, dispersion and emulsion polymerization of vinylidene chloride, production of polyether-based surfactants, continuous polymerization technology and reactor design for polyether, gas-phase ethylene polymerization with super condensing model operation, and reactor design for poly(para-phenylene terephthalamide) production used for Aramid fiber, etc.

After the reform and opening of China, some competent enterprises started to import advanced production technologies and pilot plants from the developed nations, substantially improving the quality and technical level of their products. However, they still did not understand the design principles and control laws of the processes and equipment. In order to develop new products, to scale up the production, and to renew the equipment, they often entrusted the Chinese universities to carry out research on the related principles and laws, and called this approach "digestion–absorption–renovation." SKLoChE-ZJU also involved in such projects, such as production technology and reactor design for high impact PS and polyester, complete production technology for large-scale gas-phase polymerization of ethylene, and multizone circulating fluidized bed reactor technology for olefin polymerization, etc.

Following the establishment of R&D centers and production facilities in China, more and more global leading enterprises started scientific and research collaborations with Chinese universities. In the recent years, SKLoChE-ZJU has also undertaken a number of research projects entrusted by the global leading enterprises, namely BASF, DuPont, DSM, Rohm & Hass, General Motors, Boeing, Arkema, Firmenich, etc. Unlike projects from Chinese enterprises, these projects mainly involved fundamental research, including polymerization kinetics and modeling of polymerization processes, exploratory polymerization experiments, application law of novel initiators and additives, and development of advanced materials. These companies were very concerned about details in the research progress, including technical route, experimental and/or theoretical research method, etc. and were interested in new ideas and discoveries.

The Chinese scholars often organized workshops for R&D staffs in the enterprises to introduce the research progresses in the field of PRE in China and the world. In the recent years, many companies have begun to work with the Chinese universities to recruit post-doctoral researchers, expecting them to tackle the practical problems in production or to develop new technologies for their production, and to conduct in-depth research works under the supervision of professors from the Chinese universities.

It is obvious that the Chinese academia have already established close relationships and collaborations with the industries, making important contributions to the recent advances of polymer industry in China. However, the PRE researchers in China are not solely for the application development to serve the enterprises, but also dedicated to fundamental research. It is, after all, a pleasure to do things following their own interest and enjoying academic freedom. Due to the lack of financial supports in the early time, it was very difficult to widely support the fundamental research in the field of Engineering Science. However, the Chinese government has significantly increased supports for fundamental research since the beginning of this century. This can also be seen from the funding growth at SKLoChE-ZJU in the past 15 years, as shown in Figure 2, where the research expenditure coming from the National Natural Science Foundation of China and the government departments at all levels increased by an annual average growth rate of 12.7%. Therefore, the PRE researchers in China currently work on both directions, by continuing to take the commission from the industry as well as to carry out in-depth fundamental research of global science and engineering frontier on PRE. Figure 3 shows the record of referred journal papers published by 20 full-time researchers at SKLoChE-ZJU in the past 15 years. It can be seen that, on top of the rapid increase of the total publication, the number of papers published in the international journals and in the journals with impact factors over 3 increased dramatically. In responding to the increased funding, the fundamental research on PRE at ZJU has greatly improved both on the scale and on the level.

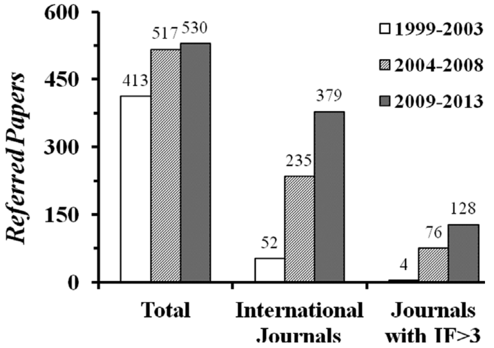

Figure 3. Journal papers published by SKLoChE-ZJU researchers during past 15 years.

These achievements are benefited not only from the increase in research funding and the upgrades of experimental instruments and equipment, but also from the close international collaborations. Currently, each of the 20 full-time researchers at SKLoChE-ZJU has either received Ph.D. degree from an international university or had overseas experience as a visiting researcher. Meanwhile, many fundamental research projects have been carried out in cooperation with global leading scholars and scientists in the PRE field. Since 2005, the SKLoChE-ZJU researchers have been fruitfully collaborating with Prof. Shiping Zhu of McMaster University.

The PRE research progress at SKLoChE-ZJU was also aided by combining fundamental research with application development, by the close connections with domestic and international leading enterprises, as well as by collaborations with world leading scholars and scientists. In fact, the PRE research in China over the past 30 years is epitomized by the development of SKLoChE-ZJU.

4. Latest Progress

For half a century, the PRE researchers have made important contributions to the development of pilot polymer production technologies, and accomplishments in tailoring chain microstructures and performance of polymer products. For example, based on modeling and simulation of polymerization kinetics, the principles for selection of different continuous polymerization reactors were developed for various polymerization reaction mechanisms.[34] The PRE researchers have also carried out the studies on the effect of micro mixing and diffusion control on the molecular weight and MWD of polymer products,[35] which provided foundation for design and optimization of process operation for industrial polymerization processes of high viscosity or involving a heterogeneous phase. For copolymerization of monomers having a relatively big difference in reactivity, the complete mixing flow mode and semi-batch operation have been applied to ensure the homogeneity of copolymer compositions during the polymerization processes,[36,37] which was based on modeling and simulation of the copolymerization kinetics. Recently, Professors Yongrong Yang and Jingdai Wang of SKLoChE-ZJU developed an ultrasonic-assisted sensing technology for online monitoring of reactor operation in complex polymerization processes.[38,39] This online monitoring helps to ensure the stability and safety of polymerization facilities and to ensure the same polymer chain structures for stable product performance.

In general, the main focus of the recent research at SKLoChE-ZJU concentrates on the precise control of polymer chain and primary aggregate structures. This focus is essential for the Chinese polymer industry, which has experienced excess production of the commodity polymer products, but severe lacking of the high-end performance polymers.

4.1. Precise Control of Polymer Chains

The polymerization of monomers to form polymer chains is a probability event with numerous reactions occurring concurrently. The chain structures of polymers are thus dominated by these probability events, leading to polydispersity of structural properties. In addition, there are many complex factors also affecting the polymerization, such as residence time distribution of different components in the reactor and the degree of micro mixing. Therefore, the chain microstructural properties of polymer product are polydispersed and are represented in a form of distribution, regardless of molecular weight, copolymer composition, and chain configuration. A small variation in these distributions may result in a huge difference in the final properties of polymer products. This also explains why polymers made from the same recipe can be tailored to possess different structural properties for desired performance, even though these polymers have similar average molecular weight and comonomer content. Unfortunately, due to the limitation imposed by the polymerization mechanisms, most polymer products are either homopolymers or random copolymers. The control on polymer chain structures could only be achieved by targeting the average polymer chain parameters. The products are therefore mainly commodity materials.

Approximately two decades ago, controlled/living radical polymerization (CLRP), such as atom transfer radical polymerization (ATRP),[40] and reversible addition fragmentation chain transfer (RAFT) polymerization,[41] was invented in academia of polymer chemistry. In the CLRP process, there exist a rapid initiation and a reversible chain transfer or termination reaction. Therefore, the life of active chains can be extended to the whole polymerization process, in the scale of a few hours. This could not only help to produce polymer chains with nearly monodispersed molecular weight, but also offer adequate time for sequence structure control of monomer units. Therefore, CLRP could be used to produce high performance or functional polymer materials.

However, there have been only a limited number of CLRP applications on a pilot-scale production reported so far, which might be due to the relatively short period for technology development after their invention. At the early stage, the studies on CLRP mainly focused on homogeneous solution polymerization. Low polymerization rates and existence of termination reactions were also some of the limitations of CLRP processes. Based on the "segregation" effect of latex particles on radicals in emulsion and mini-emulsion polymerization, which reduces radical termination and thus increases the radical concentration and polymerization rate, Luo and co-workers. of SKLoChE-ZJU studied RAFT (mini) emulsion polymerization.[42–44] The "super swelling" phenomenon was observed, which destabilizes emulsion polymerizations. A mechanistic explanation was given through thermodynamic simulation and experimental verification. With design of a special type of RAFT agents, stable and rapid RAFT (mini) emulsion polymerization was achieved for the first time, and the polymers having high molecular weight and narrow MWD were synthesized.[44,45] Following these studies, an expression to estimate the average number of radicals in latex particle was developed,[46] which could reveal the mechanism of RAFT emulsion polymerization and assist the researchers to grasp the method to control polymerization rate.

On the other hand, the chain structures that determine polymer performance in application are very complicated. It is often difficult to improve polymer performance or function by the control over MWD only. Moreover, based on the PRE principle, batch or plug flow operation should be used for CLRP to ensure narrow MWD. But in copolymerization, such an operation leads to uncontrollable gradient composition distribution in the copolymer chains due to a reactivity difference of the comonomers. Resulting polymer chains could have one end rich in active monomer, and the other end dominated by the less active monomer. Although the intermolecular inhomogeneity can be resolved by CLRP, the intramolecular inhomogeneity of individual chains remains to be challenging.

To tackle this challenge, Luo and Li et al. in collaboration with Zhu of McMaster University extended their investigation from the concentration variance of comonomers with polymerization time, which is normally considered in traditional studies on polymerization kinetics, to the concentration variance of all the polymer chain species in CLRP processes. Based on the polymerization mechanism, differential equations for all the species were established and then simplified to a finite number of differential equations for the 0th–2nd order moments using the method of moments. The equations for different polymer chain structures were thus obtained. By combining these equations with the semi-batch reactor model, the monomer addition profiles could be calculated and used to control the metering pump for comonomer feeding to tailor polymer chains for targeted molecular weight, copolymer composition, and sequential structure. As a result, polymer chains with precise control over their microstructural properties could be obtained, to achieve *digital synthesis and precision production* of polymer materials.[47–49] This model-based monomer feeding policy (MMFP) technique was further verified by RAFT solution copolymerization of styrene (St) and butyl acrylate (BA) and other monomer systems. The copolymers having random, linear gradient, hyperbolic tangent gradient, and triblock sequence structures were successfully synthesized.[50,51]

Later, the research group further investigated RAFT semi-batch emulsion copolymerization and prepared a series of tailored high molecular weight block, gradient, hyperbranched, and cross-linked copolymers. A wide variety of advanced polymeric materials with good application potential were developed. For instance, the St/BA copolymers having the same copolymer composition but with random, linear gradient, V gradient, diblock, and triblock structures were precisely synthesized. The St/BA copolymer having the V gradient structure was found to possess excellent shape memory properties.[52] By precise synthesis of a series of PS-*b*-PBA-*b*-PS triblock copolymers with different chain lengths via stepwise RAFT emulsion copolymerization of St and BA, a series of copolymers having various mechanical properties were produced. The thermoplastic elastomer having tensile strength up to 10 MPa and elongation at break over 500% was synthesized for the first time using CLRP emulsion copolymerization.[53] Moreover, polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS)[54] and polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS) triblock copolymers having high molecular weight were also successfully synthesized using RAFT emulsion copolymerization, and the polymers were found to be excellent modifiers for asphalt emulsions. Although anionic polymerization has already been used for SBS and SIS production long time ago, very few monomers can be polymerized using the ionic technique. Moreover, the technique requires the use of less safe alkyl metal compound as initiator and anhydrous and oxygen-free polymerization system, making it much more stringent than CLRP emulsion polymerization. In addition, the SBS and SIS produced by the ionic technique must be emulsified when a latex form is required for application. The CLRP emulsion copolymerization for SBS and SIS has thus a clear advantage in comparison.

Luo and co-workers[55] and Wang and co-workers[56–60] further used the MMFP technique in solution and in mini-emulsion RAFT copolymerization for tailoring hyperbranched, star, and cross-linked polymers. For example, hyperbranched polyacrylamides (PAM) were synthesized via batch and semi-batch RAFT solution copolymerization of acrylamide (AM) and *N*,*N*′-methylene-bisacrylamide (BisAM). It was found that the hyperbranched PAMs with uniform branch distribution were obtained using the MMFP technique.[56–58] Furthermore, semi-batch RAFT inverse emulsion copolymerization of AM and BisAM was carried out. The PAMs having uniform hyperbranched structures produced at a high polymerization rate could be readily used in application.[61] The hyperbranched PAMs were utilized as a polymeric RAFT agent for further copolymerization of methacryloxyethyltrimethyl ammonium chloride (DMC) to produce hyperbranched cationic acrylamide copolymers (CPAMs), which have hyperbranched PAM core and cationic PDMC shell blocks at the end of each arm. Compared to the commercial linear CPAM flocculants of high molecular weight, the hyperbranched CPAMs possessed low viscosity in aqueous solution, good shear stability, and high flocculation efficiency. Its flocculation performance in industrial wastewater treatment was superior to that of commercial linear CPAM flocculants, in which DMC units were randomly distributed in the polymer chains.[62]

In the recent years, several important progresses have been made in the areas of olefin living coordination polymerization.[63] Researchers at SKLoChE-ZJU also applied the MMFP technique in living coordination polymerization for tailoring high-performance polyolefin materials. The homopolymerization and copolymerization of ethylene using novel FI catalysts were first investigated.[64] Based on the polymerization kinetics and process modeling, PE's having bimodal MWDs[65] and ethylene/1-octylene bi/tri-block copolymers[66] were designed and synthesized by combining chain transfer or multiple-stepwise polymerization methods, respectively.

4.2. Tailoring of Primary Aggregate Structures

During the polymerization, the structures of primary aggregates in polymer not only influence the polymerization process substantially, but also affect the subsequent polymer treatment and processing a great deal, as well as the performance of final polymer product. For example, reactor granule technology (or Catalloy technology) in polyolefin polymerization[67,68] and multizone circulating reactor technology (MZCR)[69,70] provided polymer products with special primary aggregate structures via controlling monomer concentration distribution inside the reactor space and varying monomer concentration with polymerization time. In particular, the MZCR technology allowed synthesis of the polymer particles having a layer-by-layer onion-shaped structure with homopolymer in one layer and copolymer in another. The performance of the product was dramatically improved.

Recently, Feng and co-workers[71,72] of SKLoChE-ZJU developed a novel monomer-switching gas-phase reactor on the basis of stirred fluidized bed reactors. They used a periodic switching monomer feeding strategy to control the growth environment of polymer particles. This allowed the production of high-impact polypropylenes (HIPPs) in a single polymerization vessel via periodic gas switching rather than by cyclic flowing of polymer particles between two zones of a looping reactor. It was found that the switching frequency, equivalent to the number of particles recycled in a multizone loop reactor, significantly influenced the polymer structures, thus determining mechanical properties of the polymer.

Nano (hollow) capsules have been precisely synthesized by CLRP and assembled into materials with special aggregate structures. The work is very promising with a wide range of applications. Based on the characteristics of RAFT polymerization and self-assembly behavior of amphiphilic block copolymers, Luo and Gu[73,74] developed a new method for the preparation of nano capsules through interfacial RAFT miniemulsion polymerization, in which an amphiphilic block copolymer RAFT agent was used as surfactant to form mini-emulsions for monomer/core material solutions. Since the polymerization reaction was confined within the oil/water interface, the polymer chains gradually grew from the interface toward the inside of latex particle to form single polymer shell in-situ. Through this approach, the problem of morphological control, which is greatly influenced by diffusion control of polymer chains during the phase separation with the traditional method, was overcome. With this technique, it is very easy to precisely control thickness and physical properties of polymer shells on the nano scale. The preparation process is simple, highly efficient, environmentally benign, and suitable for the industrial production. The technique has been applied in preparation of monodispersed nanocapsules,[75,76] polymeric capsules having phase transition characteristics,[77] collapse-free ultrathin-shell nanocapsules,[78] and their nanoporous antireflection coatings,[79] and super thermal insulation materials.

More recently, Wang and co-workers[80,81] developed *N*,*N*′-dimethylaminoethyl methacrylate (DMAEMA) and methyl methacrylate (MMA) block copolymers (PDMs) through a stepwise RAFT solution copolymerization. The PDMs were used as polymeric surfactant for emulsion (co) polymerization of MMA and other monomers. The resulting latexes could be coagulated using trace amount alkali. The coagulated latexes could be redispersed by purging CO_2 and sonication to form stable latexes again, and the stable redispersed latexes could be re-coagulated with N_2 bubbling. Such coagulation and redispersion cycles by respectively purging CO_2 and N_2 could be repeated numerous times. The reversible coagulatable/redispersible property of the latexes synthesized with PDM polymeric surfactant is possibly due to a "riveting" effect of PDMAEMA chain segments on the latex particle surface. PDMAEMA interacts with CO_2 to form hydrocarbonate functionality, which increases the latex surface hydrophilicity and creates repulsion among the same charge, thus forcing the latex particles to disperse. N_2 washes off CO_2 from PDMAEMA, resulting in the latex coagulation.

Synthetic latex is the product of emulsion polymerization, in which water accounts for 45–60% of the total volume. Even in high solid content latex products, water still accounts for approximately 26–40%. The large proportion of water undoubtedly increases the cost of transportation and storage of the latex products. When a dry powder form is required in some applications, the latex must go through a four-step treatment process, including coagulation, filtration, washing, and drying. For the coagulation process, it is often necessary to add a large amount of acid, alkali, salt, or other demulsifier to achieve demulsification. Because the demulsifier and surfactant residues have negative impact on performance of the polymer product, they need to be removed by washing. Therefore, the coagulation process incurs high operating costs and energy consumption, along with generating a large amount of wastewater, thus raising environmental concerns. Moreover, water washing is often not very effective to remove surfactant owing to its amphiphilic property. Therefore, this technique of reversibly coagulatable/redispersible latex preparation has great potential to be applied for the development of synthetic latex industry for its low energy consumption and environmentally friendly process.

On top of abovementioned research works, SKLoChE-ZJU has established a polymer product engineering innovation research team supported by Ministry of Education of China for adapting global development in chemical engineering. We are currently working on model-based precise control of polymer product microstructure and functionality distribution toward making contributions to thefundamental of chemical product engineering theory and methodology and promoting rapid development of advanced polymer materials.

5. Conclusion

The polymer industry in China has developed rapidly over the past 30 years. The PRE researchers in China have made important contributions to the development. The PRE research in China started from the 1960's. As a pioneer of PRE in China, Prof. Zuren Pan led the research at ZJU for over 30 years. He founded SKLoChE-ZJU in this field, which has become a well-recognized research center and a base for the training of high-level talents for PRE in China. Meanwhile, such enterprises as SINOPEC and their research institutions have also developed their own core technologies with independent intellectual property in polymerization catalysis and polymerization processes through collaborations with the institutes of Chinese Academy of Sciences and Chinese universities.

Chinese researchers of PRE have been always combining scientific research with production practice. They undertake not only projects for the development of polymerization technology, and the design and scale-up of reactors from Chinese small and medium companies, but also for the "digestion–absorption–renovation" program from Chinese leading enterprises. Furthermore, they collaborate with global leading enterprises to conduct research on polymerization kinetics and modeling, exploratory polymerization experiments, and development of advanced materials.

In the early days, the research in Chinese universities mainly focused on helping the industry. With the development of economy and society, the focus has been transferred to both fundamental and industrial research. Recently, the research interest has been shifted from the optimization of polymerization process efficiencies to the precise control of polymer chain and aggregate structures. On the basis of CLRP and living coordination polymerization, a model-based monomer feeding policy technique has been developed for precise control of polymer chains. The technique was further verified by the CLRP solution and (mini) emulsion copolymerization and living coordination solution copolymerization of olefins. Some new technologies for tailoring primary aggregate structures, including interfacial emulsion polymerization and olefin polymerization with periodic gas switching strategy, were developed also. Several polymer materials with special properties or functionalities have been developed. The current PRE research in China is focusing on polymer product engineering.

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