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Polymerization Reaction Engineering: Past, Present and Future

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Summary: In this short review we describe some of the main developments of polymer reaction engineering since the early days of polymer science in the 1930's to the current challenges of today.

Keywords: polymerization catalysts; polymerization reactors; polymer reaction engineering; polymer science

Introduction

Mankind has used natural polymers such as animal skins, silk, cellulose, and natural rubber since pre-historic times. In this way, it is no exaggeration to say that polymers have helped enhance the life of mankind for the last few millennia. However, despite their usefulness, the true nature of polymer molecules was only elucidated in the beginning of the 20th century led by the pioneering work of Staudinger. Among his early contributions was the realization that polymers are not colloids, but true macromolecules with very high molecular weight, a realization that could only be achieved with the development of polymer characterization methods that are standard in any polymer quality control laboratory today. In particular, the work of Herman Mark on X-ray crystallography was instrumental to support the macromolecular theory of Staudinger. Even with almost no detailed understanding of the nature of polymers before the 1930's, exploratory laboratory experiments led to the early synthesis of polymers such as phenol-formaldehyde, urea-formaldehyde, polyesters, polyamides, polystyrene, polyvinylacetate, polyvinylchloride, polyacrylic acid, polylactic acid, polyethyleneoxide, polymethylisoprene rubber, polybutadiene, polyformaldehyde, to mention a few.[1]

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The Early Years: 1930's and 1940's

The early work up to 1930 provided the basis for an explosion of theoretical and experimental developments in the next two decades. The 1930's were rich with theoretical findings in polymer science and engineering and with the commercial production of several new polymers. These investigations would transform our understanding of polymer manufacture and culminate in the development of several continuous polymerization processes and the establishment of polymer reaction engineering as a new area of research in the 1940's.

In 1930, Kuhn[2] predicted that the chain length distribution, f_n, of fragments produced from the random scission of a polymer chain is given by the equation,

$$f_n = \alpha(1-\alpha)^{n-1} \tag{1}$$

where n is the chain length of the polymer chain fragment and α is the probability of any particular polymer bond being broken. This is the first appearance in the scientific literature of the expression that would be called later the *most probable distribution* of chain lengths and would play such a pivotal role in the development of mathematical models in polymer reaction engineering.

In 1934, Chalmers[3] proposed several mechanisms for addition polymerization and applied them in kinetic calculations for very short chains. Even though the validity of his results was limited because polymerization mechanisms were not yet well understood, his speculations stimulated other investigators to direct their attentions to this new and promising area of research.

The chain length distribution of polymers made with living polymerization was modelled by the first time in 1935 by Dostal and Mark,[4,5] assuming that the rate constants were independent of chain length. Since they did not consider the case of instantaneous initiation, they did not obtain a Poisson distribution. Instead, their solution was in the form of an infinite series of Poisson distributions, each term corresponding to the Poisson distribution resulting from chains initiated at different times:

$$P_n = \frac{k_i}{k_p}\sum_{m=n-1}^{\infty}\frac{z^m}{m!}e^{-z}; \quad z = \int_0^t k_p[M(t)]\,\mathrm{d}t \tag{2}$$

The leading moments and averages for molecular weight distributions that would later become the standard way of describing molecular weight distributions (number-, weight-, and z-average molecular weights: M_n, M_w, and M_z) were first defined in 1935 by Kraemer and Lansing.[6,7] They showed that the explicit distribution as well as the three molecular weight averages could be determined from centrifuge experiments. They also pointed out that M_n could be calculated from osmotic pressure and M_w from viscosity measurements, and discussed at length possible measures of the chain length distribution (CLD), including the use of the ratios of the moments of the CLD that we use today.

In 1935, G. V. Schulz, unquestionably one of the giants of polymer science and engineering, used statistical methods to derive the CLD for monomer-terminated addition polymerization assuming a constant probability of propagation, α, and long polymer chains. He obtained the now well-known most probable distribution[8] sometimes called the Schulz-Flory distribution:

$$f_n = (-\ln\alpha)\alpha^n = \frac{1}{\bar{x}_n}\exp\left(-\frac{n}{\bar{x}_n}\right) \tag{3}$$

His long chain approximations, $n \cong n-1$; $1-\alpha = \frac{1}{\bar{x}_n} = -\ln\alpha$, are used today to allow alternative representations of the most probable distribution (cf. Equations 1 and 3). Schulz also showed that this distribution had a polydispersity of 2. This result requires that the rate constants be independent of chain length and that α be constant over the lifetime of a living polymer chain, providing *instantaneous distributions* for living chains. Although his paper was published in 1935, Schulz comments that the work had been completed a year earlier; he had delayed publication because he thought no one else was working in this field. Later in 1937, Schulz and Husemann[9] showed that the Bodenstein stationary-state approximation (quasi-steady state) could be applied to free-radical polymerization.

In 1935-1936, another giant in our field, Paul Flory derived the CLD for linear condensation polymers based on statistical arguments.[10,11] His main assumptions were: 1) rate constants are independent of chain length; 2) no addition or removal of polymer and reactants from the reactor; 3) reaction conditions may vary during polymerization. He showed that for A-B and AA-BB condensations with equal stoichiometry and a fraction p of the functional groups reacted, the CLD is given by once again the most probable distribution:

$$f_n = (1-p)p^{n-1} \tag{4}$$

He also provided concise expressions for the MWD averages:

$$M_n = \frac{M_0}{1-p}; \quad M_w = M_0 \frac{1+p}{1-p}; \quad M_z = M_0 \frac{1+4p+p^2}{(1-p)^2} \tag{5}$$

For unequal stoichiometry, Flory proposed an elegant modification of Equation (4), by defining $r = \frac{[A]}{[B]}$ and substituting p by $pr^{1/2}$:

$$f_n = (1 - pr^{1/2})(pr^{1/2})^{n-1} \tag{6}$$

In 1937, Flory addressed the problem of vinyl polymerization and proposed a mechanism which included transfer to monomer and termination by both combination and disproportionation.[12] Flory treated several important aspects of polymer reaction engineering in this seminal paper, including: 1) the description of chain transfer to monomer, solvent, or other chemical species; 2) the derivation of models for monomer conversion in batch reactors and determination of kinetic parameters for initiation, propagation, and termination for several monomers; 3) the definition of the kinetic chain length; 4) the description of chain transfer to polymer and consequences for long chain branch formation; 5) the explanation of how dead chains with terminal double bonds can be polymerized forming long chain branches; and 6) the estimation of heat of polymerization for several monomers.

The kinetics and CLD of reversible polycondensation was investigated by Schulz in 1938.[13] He showed that the chain length of condensation polymers is limited by equilibrium and derived a general relationship between the equilibrium constant, the condensate content, and the chain length. He found that the equilibrium CLD was once more the most probable distribution. In this work, Schulz also presents batch reactor modeling equations for the evolution of average chain length over time.

In the following year, Schulz studied the kinetics and CLD of addition polymerization with various degrees of coupling,[14,15] including termination by combination and higher levels of coupling as might occur with diradical initiators. He also derived a general CLD for any degree of coupling, given by the expression,

$$f_n = \frac{(-\ln \alpha)^k}{k!} n^{k-1} \alpha^n \tag{7}$$

where $k = 1$ for termination by disproportionation and $k = 2$ for termination by combination. He also defined a new measurement of nonuniformity of chain length, the *Uneinheitlichkeit*, U, defined as follows:

$$U = \frac{M_w}{M_n} - 1 = \frac{1}{k} \tag{8}$$

In this work, Schulz also derived the CLD for equilibrium addition polymerization and obtained the most probable distribution.

It is remarkable that during the decade from 1930 to 1940 we moved from practically no knowledge of polymerizaiton kinetics and chain length distributions to a good understanding of these issues for both polycondensation and addition polymerization. The same decade saw an explosion of new commercial polymers (polymethyl methacrylate, polystyrene, polyethylene, to name just a few) with synthesis based on this new understanding of how to control batch polymer characteristics.

The knowledge of polymer chemistry continued to grow rapidly in the 1940s, accompanied by the emergence of basic polymer reaction engineering principles. The well-known Poisson distribution for living polymerization under instantaneous initiation was developed by Flory in 1940 and applied to the polymerization of ethylene oxide:[16]

$$f_n = e^{-\bar{x}_n} \frac{(\bar{x}_n)^{n-1}}{(n-1)!} \tag{9}$$

The autoacceleration or Trommsdorff effect was also elucidated in the 1940's. Schulz and Blanschke noted the autoacceleration phenomenon in the polymerization of methylmethacrylate at higher conversions in 1941.[17] Trommsdorf and coworkers[18,19] explained this effect due to a decrease in radical termination reactions at high viscosities and conversions. The effect and its explanation was also later discussed by Burnett and Melville.[20]

Equations describing copolymer composition were first developed by Dostal[21] in 1936, but he did not complete his analysis to obtain a final expression for instantaneous copolymer composition (F_i) and sequence length distributions (S_{1n} is the fraction of sequences of monomer-1 units with length n, and $\bar{S}_1$ is the average sequence length) in terms of monomer reactivity ratios (r_i) and monomer composition (f_i). In 1944, these equations were derived simultaneously by Alfrey and Goldfinger,[22,23] Mayo and Lewis,[24] and Wall for the terminal model:[25]

$$F_1 = \frac{(r_1 - 1)f_1^2 + f_1}{(r_1 + r_2 - 2)f_1^2 + 2(1 - r_2)f_1 + r_2} \tag{10}$$

$$S_{1n} = (1+\alpha)\left(\frac{\alpha}{1+\alpha}\right)^{n-1}; \quad S_{2n} = (1+\gamma)\left(\frac{\gamma}{1+\gamma}\right)^{n-1}$$
$$\bar{S}_1 = 1+\alpha; \quad \bar{S}_2 = 1+\gamma \tag{11}$$
$$\alpha = \frac{r_1 f_1}{1-f_1}; \quad \gamma = \frac{r_2(1-f_1)}{f_1}$$

The understanding of the chemical composition of linear binary copolymers was further extended when Stockmayer derived the bivariate distribution for chain length and chemical composition in 1945:[26]

$$w(n,y) = \exp\left(-\frac{n}{\bar{x}_n}\right)\frac{n}{\bar{x}_n{}^2}\sqrt{\frac{n}{2\pi F_1(1-F_1)\kappa}}\exp\left(-\frac{ny^2}{2F_1(1-F_1)\kappa}\right)$$
$$\kappa = \sqrt{1-4F_1(1-F_1)(1-r_1r_2)} \tag{12}$$

where $w(n,y)$ is the weight distribution of chains of length n and composition y. The parameter y is the deviation from the average molar fraction of comonomer 1 in the copolymer, F_1.

In 1947 Denbigh[27] published a remarkable paper which might be considered the first paper on modern polymer reaction engineering. In his comprehensive contribution, he noted that all the earlier work on batch reactors applied directly to continuous tubular reactors with the length replacing time as the independent variable. He then developed equations for polymer production rate and the CLD for polymerizations in continuous stirred-tank reactors (CSTR), covering both living and non-living polymerizations. He also showed that, for polymerizations such as free-radical with a short chain lifetime, the CSTR gives narrower CLDs than batch reactors, while for polymerizations with chain lifetimes comparable to the reactor average residence time or longer, batch reactors will produce polymers with narrower CLDs than CSTRs. Denbigh also pointed out that the instantaneous CLD is identical to the exit CLD in a CSTR operated at steady state, but in batch or tubular reactors, the final CLD is composed of all instantaneous CLD weighted by their respective instantaneous polymerization rates. He also suggested the use of a train of CSTRs to overcome the lower average polymerization rate of a single CSTR, and to narrow the breadth of the CLD for polymerizations with a long chain lifetime.

In the period from 1945-1949, the foundations for the understanding of emulsion polymerization were laid by Harkins[28-30] and Smith and Ewart[31-33], including the description of the interactions between monomer droplets, micelles, and polymer particles. These papers provide much of the basis of our current understanding of emulsion polymerization processes. Long before publication, these results were used in the early 1940's to help design and operate styrene-butadiene rubber plants. In addition, the 1940's saw the introduction of a range of new commercial polymers (fluoropolymers, ABS, epoxies, polyester and acrylic fibers, etc.) and process technologies (high pressure autoclave and tubular reactors for polyethylene, series of CSTRs for emulsion polymerization, tubular reactors for polyamides, etc.).

The Developing Years: 1950's to 1980's

The period from 1950 to 1990 saw the continued growth and evolution of process technologies, largely stimulated by the combination of polymer reaction engineering principles with the fundamental understanding of polymerization kinetics developed in the earlier years. In addition, the introduction of new "inorganic" catalysts led to additional process developments and large scale production of new polymers such as high density polyethylene and polypropylene. These advances are well-known to many readers, and will be only be briefly outlined here.

Challenges in the design and operation of large-scale industrial reactors, due to the stringent requirements for the removal of heat of polymerization, led to several new creative reactor designs and operation conditions such as development of tubular and loop reactors, use of external recycle lines for heat removal, implementation of evaporative cooling, and use of suspension and emulsion polymerization processes. These new operation conditions could involve multiple steady states and sometimes sustained oscillations in many semi-batch and continuous reactors, leading to the need of extraordinary safety measures in design and operation to avoid thermal runaway. Understanding the dynamic behaviour of polymerization reactors became of paramount importance, stimulating theoretical developments in the area of mathematical modeling, and reactor optimization and control.

The many innovations in polymer reaction engineering during these four decades included the development of:

- Slurry reactors for polyethylene and for polyacetals
- Slurry loop reactors for polyethylene and polypropylene
- Gas phase stirred-bed reactors for polypropylene, ethylene/propylene copolymers and polyesters

- Fluidized bed reactors for polyethylene, polypropylene, and its copolymers
- Tubular reactors for polyacetals, polyesters, and rubbers
- Tower reactors for vinyl polymers and polyesters
- Suspension and emulsion polymerization processes for vinyl polymer

Because of these advances, the commercialization of many new polymers became possible: high density and linear low density polyethylene, isotactic polypropylene, ethylene/propylene and ethylene/propylene/diene rubbers, isotactic polybutadiene, spandex fibers, polyimide resins and fibers, new epoxies, aromatic polyamides, polycarbonates, polyformaldehyde and its copolymers, new adhesive and foam polymers, etc.

New Challenges: 1990 – 2003

The last 15 years saw fewer new polymerization processes, but many process improvements designed to improve product quality, increase safety, and reduce costs. Also in this period, there were many innovations in catalysts and kinetic mechanisms in order to produce polymers with designed molecular architectures to meet specific performance demands. Existing polymer families, while continuing to expand markets through improvements in process technology and enhanced product formulation, have become high-volume commodities. The challenge for polymer reaction engineering practitioners is to continue supporting and improving existing polymer technologies while also contributing to the development of novel materials via new or improved synthetic routes.

The *Polymer Reaction Engineering V* conference, held from 18-23 May 2003 in Quebec City, Canada, brought together over 100 researchers from academia and industry to discuss these challenges and to review recent advances in the field. Many of the conference presentations have been written in article form for this *Macromolecular Symposium* volume. New modeling and measurement methodologies to study polymer systems continue to emerge, and we select a few of these contributions to highlight some of the current activity in this area:

- Pulsed-laser experimental methods have been used to measure free-radical propagation and termination rate coefficients of many important monomers and to understand the complexities of copolymerization kinetics.[34]

- Computational chemistry techniques are also now applied to probe polymerization kinetics. Although not yet reliable for quantification of rate coefficients, they can provide good estimates of activation energies and relative reaction rates: Michalak and Ziegler[35-36] have applied density functional theory calculations to estimate activation barriers and to gain considerable understanding of the chain insertion and isomerization mechanisms of the Brookhart late transition metal polyolefin catalysts.[37] When couple with Monte-Carlo simulations for polymer chain structure, these techniques have the potential to help design polymer chains with controlled chain microstructures.
- An improved equation-of-state treatment provides an excellent representation of the thermodynamic properties, including cloud-point pressures, of many important industrial polymer systems.[38]
- High throughput tools have been developed to accelerate the experimental discovery of new polymerization catalysts and product grades, and even to aid in process development.[39] The implementation of these screening tools is also leading to the development of rapid analytical techniques for polymer systems.
- Modeling of full MWDs is becoming more and more common, due in large part to the emergence of the PREDICI® software package.[40] Comparison with experimental results allows for better model and mechanistic discrimination.[41] Several papers in this issue of *Macromolecular Symposia* deal with control and modelling of MWD.
- Advances in computational fluid dynamics (CFD) continue, leading to better understanding of complex mixing/reaction phenomena such as decompositions in high-pressure ethylene free-radical polymerization systems[42] and of particle agglomeration and breakage in multiphase gas-solid fluidized bed polyolefin reactors.

This list illustrates some of the recent advances important to polymer reaction engineering practitioners. In order to make an impact on established polymerization processes, a combination of these new experimental and modeling techniques may be required. Application of these techniques not only leads to improved models of polymerizing systems, but can also lead to the discovery of "new" kinetic mechanisms that control polymerization rate and properties. Although a challenging task, such advances are occurring. Recent examples include improved mechanistic understanding for the high-temperature production of styrenic polymers,[43] emulsion polymerization of acrylic monomers,[44] and polymerization with novel coordination catalysts including detailed description of the chain walking mechanism.[45]

The past 15 years has also seen the emergence of exciting new polymerization chemistries. *Living* or *controlled* free-radical polymerization can produce polymer with narrow molecular weight distributions and block copolymers for a very broad range of monomers, allowing many new products to be designed. The last decade has also seen a revolution in the development of new classes of organometallic catalysts that have enhanced capability to control polymer microstructures. Catalyst families such as metallocenes and late transition metal catalysts are capable of producing polymers with new properties using conventional monomers. Particularly attractive is the use of two or more single-site catalysts for the production of polymers with controlled distributions of molecular weight, chemical composition, and long chain branching.[46,47] Even more dramatic examples are catalysts capable of producing polymer chains which form into rings or other more complex structures[48] or catalysts which can allow simultaneous ionic and living free-radical polymerization yielding new block copolymers not possible through a single mechanism.[49]

Most of the publications in these new areas have focused on catalyst and product design. Producing these materials in quantity at a reasonable cost provides a new challenge for polymer reaction engineering. Some progress has been made towards this goal by combining controlled polymerization chemistry with micro- and miniemulsion systems, as outlined by Cunningham,[50] and Apostolo et al.[51] The latter describes kinetic modeling used to support the application of controlled polymerization for industrial production of fluorinated copolymers. Novel chemistry is also finding its way into polymer dispersants and binders used in automotive coatings.[52]

Some Thoughts for the Future

Although many polymers are now considered commodity materials, continued development of new experimental and modeling techniques will lead to incremental process improvements and growth of product families, driven both by market forces and by changing environmental regulations. Polymer reaction engineers will lead this effort, continuing to build on the strong foundations laid by the pioneering polymer scientists in the 1930s and 1940s.

In addition, the continued developments in catalysis will create many future challenges, with the emphasis on low cost, high quality production of specialty polymers with high value. The following quote from a recent report entitled "Opportunities for Catalysis Science in the 21th Century" (Report of the Workshop, Gaithersburg, Maryland, May 14-16, 2002, page 63) illustrates well the challenges and opportunities ahead of us: "One of the *grand challenges* in catalysis is to identify multifunctional catalyst systems that carry out multiple chemical reactions in one pot to give useful complex molecules from simple feedstocks."

Processes for new classes of polymers will require our expertise and creativity to produce products with novel chain structures including hyperbranched, dendritic, and cyclic chains, as well as polymers with mixed chemical and biological building blocks. Advances in nanotechnology will call on our services for synthesis of small tailored polymer chains or chain segments that self-assemble or attach to surfaces, in-situ synthesis on a chip of designer polymers, and polymers with chemical character that allows patterning. We are convinced that these processes, while on a much different scale than traditional polymer production, will require more than ever before a detailed understanding of polymerization kinetics combined with fundamental reaction engineering principles.

Nomenclature

f_n	number chain length distribution
F_1	average molar fraction of comonomer 1 in the copolymer
f_1	molar fraction of comonomer 1 in the reactor
k_i	initiation rate constant
k_p	propagation rate constant
$M(t)$	monomer concentration as a function of time
M_o	molar mass of the repeating unit
n	chain length
p	fraction of functional groups reacted during condensation polymerization
P_n	number chain length distribution (Poisson)
r	molar ratio [A]/[B], where [A] and [B] are the concentrations of functional groups (condensation polymerization)
r_1, r_2	reactivity ratios for monomer 1 and 2
S_1	average sequence length of monomer 1
S_{1n}	fraction of sequences of monomer 1 with length n
t	polymerization time
$\overline{x}_n$	number average chain length
y	composition deviation from average copolymer composition
z	defined in Eq. (2)

Greek letters

α	probability of breaking a polymer bond, Eq. (1), probability of propagation, Eqs. (3) and (7), copolymer equation parameter, Eq. (11)
γ	copolymer equation parameter, Eq. (11)
κ	Stockmayer's bivariate distribution parameter, Eq. (12)

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