

Chemical Engineering of Polymer Dispersions

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Abstract: The research activity on dispersed polymers – polymer particle size from tens of nanometers to hundreds of microns – carried out at ETH in our group is reviewed with a brief summary of the various projects currently in progress. These have been organized into two main categories: *Polymer Reaction Engineering*, where polymerization reaction and reactor operation and control are involved, and *Colloidal Engineering*, focused on the control of particle size distribution and development of special latex post-treatment processes, such as gelation.

Keywords: Aggregation · Dispersions · Gelation · Kinetics · Polymerization

Polymer Reaction Engineering

Detailed Kinetic Modeling

The focus of polymer reaction engineering is currently on free radical polymerization in emulsion. A key feature of this process is the segregation of the active chains into extremely small reaction loci, the polymer particles. This segregation, usually also indicated as ‘compartmentalization’, explains the reduced probability of radical termination and, therefore, the large polymerization rates and molecular weights typical of this heterogeneous polymerization process. As part of the research activity of this and other groups over the years, several modelling approaches, mainly based on various types of population balance equations, have been developed to properly simulate the kinetic behaviour and the various molecular characteristics of the polymer chains produced in emulsion [1]. In this project, mathematical models are developed for branched and cross-linked polymers, in order to analyse the interplay between active chains segregation and non-

linear chain growth [2]. As an example of a typical result of such an analysis, let us consider a system where branching by chain transfer to polymer and bimolecular termination by combination are operative. Under these conditions a so-called ‘gel’ polymer is formed: it is a polymer with extremely high molecular weight and practically insoluble in any solvent, usually considered an off-spec product (not to be confused with the physical gels discussed later). According to the model prediction, the conversion where the formation of gel polymer becomes significant (the so-called gel-point) results to be much larger than the corresponding value in bulk polymerization, as shown in Fig. 1. This finding agrees with the experimental results for a branching monomer like butyl acrylate [3], where the conversion value corresponding to the on-set of gel formation roughly increases from 10% of conversion in bulk to 80% in the equivalent emulsion process. Moreover, successful predictions of molecular weight distributions have been achieved for different monomers such as vinyl acetate and vinyl chloride [3], which provide a significant validation of the model capabilities. Currently this project is focused on deepening the mechanism of gel formation in free radical polymerization, through a detailed characterization of the highly branched polymer formed in the emulsion polymerization of butyl acrylate obtained by combining different techniques (*i.e.* fractionation, GPC, light scattering

and FFF chromatography). The final objective is to use the developed models to scale the polymerization conditions to the industrial scale, in order to produce materials tailored to specific properties.

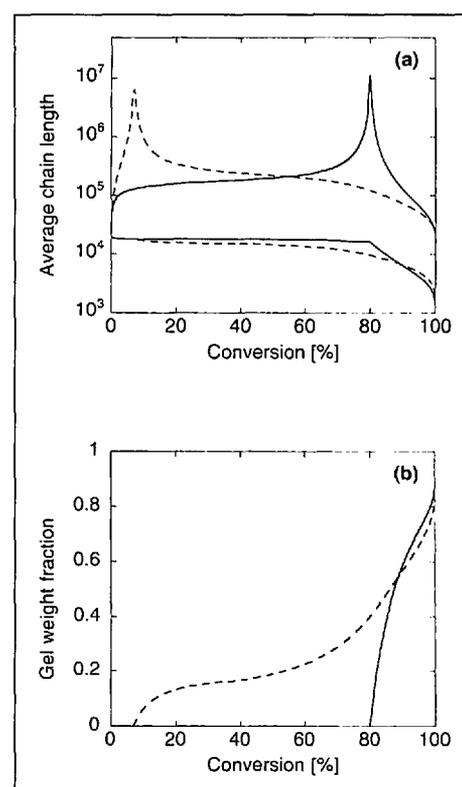


Fig. 1. Average molecular weights (a) and gel weight fraction (b) as a function of conversion in the case of chain branching occurring through transfer to polymer and bimolecular termination by combination [3]. Calculated curves: - - - bulk process; — emulsion process.

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On-line Characterization Techniques

A key tool towards a successful control of polymerization reactors is the reliable on-line monitoring of the reaction evolution in terms of polymer amount (conversion) and properties (*e.g.* particle size, molecular weight). In the case of polymer particles dispersed at colloidal level, this is not an easy task and the development of such sensors is a field of active research. A project focused on ultrasound velocity and attenuation measurements to monitor on-line and *in situ* polymerization reactors is currently in progress. The first application was conversion monitoring by a simple single-frequency sensor. In this case, the velocity of a sound wave travelling through the suspension was measured and the polymer content was estimated after a suitable calibration [4]. The resulting monitoring of conversion is reliable and the sensor is robust and is being used at the industrial scale [4]. On the other hand, the sound attenuation (*i.e.* the energy loss experienced by the sound wave travelling through the suspension) is affected by both polymer content and particle size. Since this attenuation is different at different particle sizes and sound frequencies, in principle the distribution of the

particle size can be extracted from an attenuation spectrum (attenuation as a function of the sound frequency for a sufficiently large range of frequency values) if a suitable model of sound propagation in dispersed media is available. This technique is very attractive from the practical point of view since it is not limited to highly diluted systems (like in the case of light scattering) and it is able to work up to a polymer content of about 40–50% vol., thus covering the industrial concentration range. In this project a commercial unit developed by Malvern (UK) is used to estimate *in situ* size distribution of dispersions of polymeric and inorganic solid particles. A major effort has been made to develop a mathematical model describing all main attenuation mechanisms operative in dispersed systems. The resulting model, based on the core-shell idea, is a new version of the classical single-particle model [5] extended to account for the high concentration values typical of industrial applications. While successful applications to systems with high density contrast have been reported (solid powders, PTFE latexes; see Fig. 2), problems remain in understanding the attenuation behaviour of more conventional polymer latexes (like polystyrene or polyvinylchloride) at low frequencies [6].

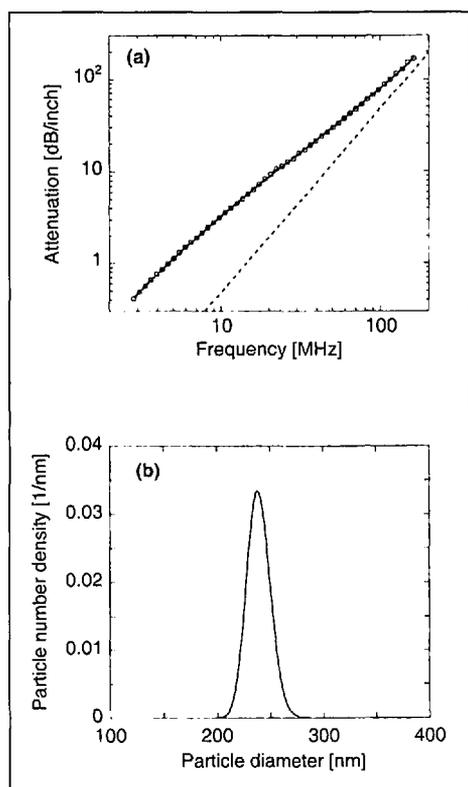


Fig. 2. Attenuation spectrum (a) and estimated particle size distribution (b) of a PTFE latex (250 nm in diameter as measured by light scattering). O experimental data; — calculated attenuation curve; --- calculated attenuation for pure water.

Living Free-Radical Polymerization in Emulsion

Since its first appearance at the beginning of the '80s, several applications and developments of this novel polymerization mode have appeared, especially in the last few years [7]. The main idea is to reversibly trap most of the growing chains by adding 'trapping species', so as to reduce the radical concentration at an extent suitable to prevent bimolecular terminations. In this case, the chains are experiencing a series of frequent activation-deactivation reactions, propagating in the first case and waiting without further reaction ('dormant state') in the second one. As a result, if the chains are generated during a short initial period of the reaction, they grow homogeneously all along the reaction (in contrast to the very short chain lifetime typical of classical free-radical polymerization) and a very narrow molecular weight distribution is obtained. Moreover, the same approach can be applied to copolymers, thus making it possible to produce block copolymers by free radical polymerization by proper sequencing of the monomer additions. Many applications of this polymer-

ization technique have been reported in homogeneous processes (bulk and solution) [7]. This project is focused on the combination between the living polymerization mode and the intrinsic ability to reduce termination achieved in an emulsion process by radical segregation. While a very low radical concentration is in fact needed in homogeneous processes (resulting in correspondingly too low reaction rates), larger concentrations of active chains can be used in emulsion polymerization, thus increasing the process productivity. Moreover, a specific study based on simulation models has indicated that only the living mechanisms not affecting the overall concentration of the active chains (like degenerative transfer or RAFT [7]) can be used in combination with chain segregation, to yield high productivity living emulsion polymerization process. This finding has been confirmed experimentally with various monomers and living agents [8]. As an example, the performance of the living polymerization of styrene in miniemulsion is shown in Fig. 3, where conversion *vs.* time, and average molecular weight and polydispersity *vs.* conversion are reported, using potassium peroxydisulfate as initiator and a specifically synthesized dithioester as RAFT agent. The use of miniemulsion instead of a standard *ab initio* emulsion, is motivated by the need of homogeneously distributing the RAFT agent among the polymer particles from the very beginning of the reaction, which can be achieved in miniemulsions without problems of transport of this compound from the droplets to the reaction loci through the aqueous phase. The observed rate of reaction is much larger than that of the equivalent bulk living process, where more than 20 h are typically needed to reach the same final conversion. Moreover, the living behaviour of the process is clearly indicated by the linear evolution of the number average molecular weight with conversion, along with the constant, low value of the distribution polydispersity. Similar results have been obtained for various monomers as well as for methyl methacrylate-styrene copolymerization, thus indicating a significant potential for the industrial application of living free-radical polymerization in emulsion [8].

Dispersion Polymerization in Supercritical Carbon Dioxide

Polymerization processes in supercritical solvents can be very attractive since the continuous phase exhibits

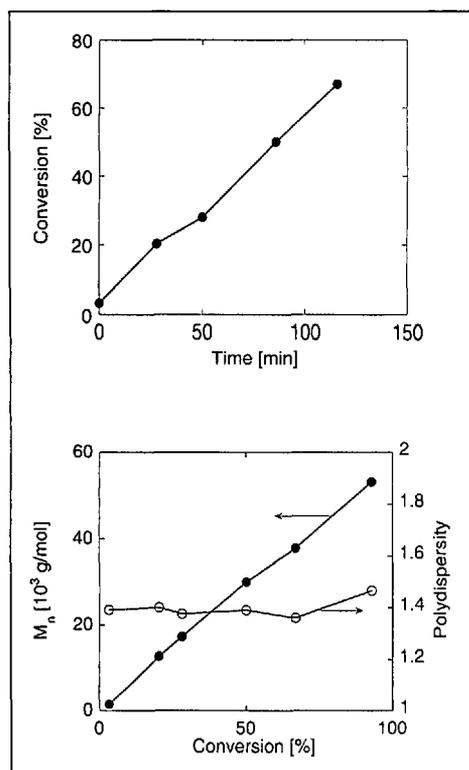


Fig. 3. Experimental values of conversion vs. time and number average molecular weight (M_n) and polydispersity vs. conversion for the living polymerization of styrene in mini-emulsion.

unique properties, such as liquid-like density, solvent strength tunable by pressure and temperature, and plasticizing effect on glassy polymers. Moreover, there are additional practical advantages such as low-cost, non-toxicity, non-flammability, easiness of removal, and environmental compatibility which could make CO_2 the future reaction medium for several polymerization processes [9]. For this to happen it is however required that we better understand the polymerization mechanisms in supercritical conditions so as to design operating conditions suitable for the efficient production of materials with desired application properties. Since the solvency power of CO_2 is quite good for small molecules such as typical monomers and very poor for most polymers (with the important exception of fluorinated polymers), particle stabilization is needed to obtain attractive polymerization rates and morphology control. Specifically designed steric stabilizers are typically used [9]. In a project focused on this polymerization mode, we are developing a comprehensive mathematical model which describes the complex interplay between phase behaviour and kinetics of particle nucleation and polymer chains formation. Phase partitioning is described using the San-

chez-Lacombe equation of state, while a coagulative nucleation mechanism is considered to evaluate the rate of particle formation and the corresponding size distribution. On the experimental side, a stirred, constant-temperature reactor with 500 ml volume is used, with careful monitoring of the charged amounts of all ingredients. The reaction evolution is presently monitored in terms of pressure variation, although the possibility of using ultrasound sensors is being considered. Preliminary experiments with methyl methacrylate as monomer have been carried out to analyze the role of the initial amount of stabilizer (Krytox 157 FSL, a carboxylic acid terminated perfluoroether with molecular weight of 2500 Da) on the particle size distribution and morphology, using AIBN as thermal initiator. The measured data are being interpreted with the developed model.

Colloidal Engineering

Control of Particle Size Distribution

The quality and performance of polymer powders is largely determined by the size and morphology of polymer particles as they result from the various stages of their industrial production. After leaving the reactor where they are synthesized, polymer particles usually undergo several coagulation (aggregation) steps in order to achieve a particle/aggregate size distribution suitable for the final steps of filtration and drying, which lead to the final powder product. Temporary stability of the polymer latex is assured by electrostatic or steric repulsive interactions between particles. Repulsive interactions are modified by process conditions during polymer synthesis, post-synthesis treatment or further processing. For example, fluid flow, temperature or concentration changes may lead to partial losses of colloid stability and subsequent aggregation to various extended structures. Depending on the operating conditions, the resulting aggregate morphology might be one of the following: 1) a latex or slurry with significantly larger particle size, 2) a large dense aggregate, a so-called coagulum, 3) a gel. In order to obtain industrial products which meet specific application properties, we need to control the structure and the kinetics of formation of these extended solid structures, and to be able to scale up the corresponding operating conditions.

In this context we aim at a rationalization of the aggregation behavior of latexes as a function of processing conditions.

We experimentally study aggregation kinetics and structure of aggregates formed in latexes destabilized either electrostatically or by shearing, using carefully controlled flow regimes in laminar, transition and turbulent regions. We separately focus on conditions leading to products at two vastly different lengthscales: latex or slurry of larger particle size as produced by a coagulation unit on one hand, and gel or coagulum on the other. We use a unified approach based on population balance equations [10] to model particle size distribution in industrially relevant, *i.e.* relatively concentrated, systems. Separate terms in the population balance equations can account for particle nucleation and growth due to polymerization, in addition to describing particle aggregation and breakage. Strategies for efficient solution of the population balance equation are available [11] once the collision kernel – the matrix of aggregation rate constants – is known.

We used this approach to simulate aggregation in polyvinylchloride, polystyrene and polyvinylacetate latexes [12], in good agreement with experimental data. Evolution of particle size distribution during the emulsion polymerization of polyvinylchloride was studied (Fig. 4), including nucleation and growth terms in the population balance equation [13]. A comprehensive kinetic scheme was considered to describe the polymerization reaction both in aqueous and particle phase. Along with standard reactions such as initiation, propagation and terminations, different branching mechanisms have been included to allow the simulation of systems with nonlinear polymer chains. The calculated polymerization behavior compared favorably with the experimental data on conversion and molecular weight distribution.

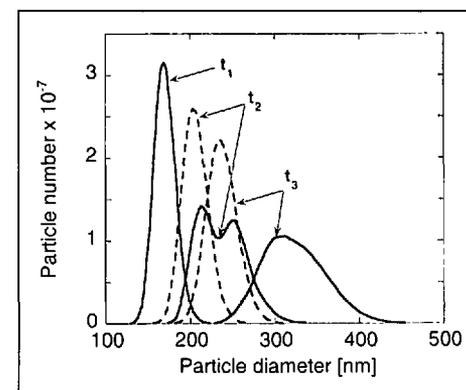


Fig. 4. Particle size distribution during emulsion polymerization of vinylchloride. Calculation with (—) and without (---) aggregation. $t_1=168$ min, $t_2=210$ min, $t_3=420$ min.

Aggregation Kinetics

The evolution of the particle size distribution of a dispersed system can be described through appropriate models based on population balance equations, whose reliability is largely determined by the adopted particle aggregation model. In the classical approach by Smoluchowski, later modified to account for interparticle interactions [14], the aggregation rate constants for spherical particles are given for two limiting regimes: diffusion driven (perikinetic) and simple shear flow driven (orthokinetic). Effects of fluid flow on particle aggregation below the turbulent eddy scale were previously modeled using trajectory analysis. However, these simplified approaches have not been satisfactory for proper understanding and description of aggregation phenomena [14].

We used the convection-diffusion equation describing the relative motion of a pair of particles embedded in a turbulent eddy inside a well mixed vessel to derive more realistic particle aggregation rate constants [15]. This equation, also called the pair probability equation, simultaneously accounting for the three main mechanisms of particle transport (Brownian diffusion, interparticle interactions, convection by fluid flow), was solved numerically and the aggregation rate coefficients for a pair of colliding particles were obtained as a function of particle sizes, turbulence intensity (Fig. 5), particle surface potential and ionic strength. Using the model, the complex interaction among the different aggregation mechanisms can be analyzed. For example, it can be seen that the additivity rule (*i.e.* a simple linear combination of the two limiting expressions for aggregation rate constants) cannot be used and different approaches for the intermediate

region between perikinetic and orthokinetic regimes have to be adopted.

This modeling activity is supported by experimental studies of particle aggregation, where the aggregate size and structure is monitored in polymeric latexes as a function of time and processing conditions, both in static conditions and under well-defined shearing in various flow regimes. Aggregation rate constants can be first estimated by properly interpreting the obtained experimental data, and then related to surface properties, aggregate structure and flow conditions using detailed physicochemical models [15].

Kinetic Studies of Gelation Processes

Similar to other colloidal systems, latexes produced in emulsion polymerization, when aggregating at high particle volume fractions, may form a gel, *i.e.* a continuous three-dimensional network with highly open structure. Such a structure, with dominant liquid volume and cohesive properties, makes these physical gels interesting for many potential applications, such as adsorbents, membranes for separation, ion exchange and filtration, intermediate states for polymer post treatment, *etc.* This motivates our interest in understanding the structure of these systems and in learning how to control it for engineering applications.

One important aspect in this respect is the gelation kinetics. At low particle volume fractions, aggregation is generally studied within the framework of the Smoluchowski theory, applicable to both fast and slow aggregation processes, where the stability ratio is used to account for interparticle interactions [14]. This kinetic approach gives a mean field description of the aggregation process and assumes no space correlations between particles. This assumption is reasonable only in the case of dilute solutions. An alternative approach [16] is to use percolation theory to interpret the gel structure. However, it is difficult to include in this context the kinetics of the process, which is essential for engineering applications.

Another important aspect of the gelation process is its strong dependence upon the spatial structure of the aggregates. In some recent studies (*e.g.* [17]), some initial attempts have been made to introduce structure parameters of aggregates into the aggregation kinetic kernel of the Smoluchowski equations. However, in order to interpret our experimental data on gelation kinetics, further work is

needed to understand how to construct a suitable aggregation kernel that includes information on aggregate size and structure. Thus summarizing, our knowledge of the fundamentals of the gelation kinetics is rather limited and has to be significantly improved in order to exploit the potential of gelation processes in industrial applications.

Characterization of Aggregates and Gel Structure

The structure of particulate gels is highly disordered, but at least at some length scales they are often self-similar and can be described in terms of fractal geometry, defined by an average cluster size and a fractal dimension. To characterize the structure of gels, the most commonly used techniques are those based on rheological measurements [18]. In these cases, one needs a model, the so-called scaling theory, relating the structure of gels to the rheological properties. Among the various models available in the literature (*e.g.* [18][19]), the most commonly used one is probably the model developed by Shih *et al.* [18], which defines two limiting gelation regimes: the strong-link regime at low particle concentrations and the weak-link regime at high particle concentrations. For example, by changing the particle concentration, it is possible to move smoothly from one regime to the other, thus obtaining intermediate situations, for which it is necessary to further develop appropriate scaling models. Along these lines, a new scaling model has been recently developed [20], which allows to estimate the fractal dimension in any gelation regime, based purely on rheological properties (*i.e.* storage modulus and limit of linearity), without resorting to other types of measurements. In particular, the model contains an effective microscopic elastic constant, which represents the relative importance of inter- and intra-floc links and can be estimated directly from the rheological data.

Another technique used to describe the structure of aggregates and gels is light scattering. It allows us to monitor the aggregation kinetics during the gelation process by measuring the hydrodynamic radius of aggregates using the dynamic light scattering, and the fractal dimension and the radius of gyration using the static light scattering. Our experimental activity on structure characterization is coupled with development of gelation kinetics models, since structure and kinetics are intimately related in gelation phenomena.

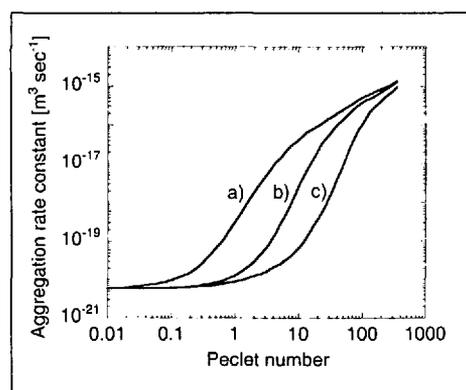


Fig. 5. Aggregation rate constant as a function of the Peclet number for three latexes with the same stability ratio but different thickness of the electrical double layer. a) $\kappa^{-1} = 83$ nm, b) $\kappa^{-1} = 9.6$ nm, c) $\kappa^{-1} = 2.3$ nm.

Control of Gelation Processes

For a given polymer latex, gelation rate and gel structure depend on many operation parameters, such as ionic strength, temperature, particle volume fraction, shear stress, etc. In the case of slow gelation, *i.e.* the kinetically controlled aggregation, it is easy to control the gel structure to a certain extent by properly altering the operating conditions. However, with respect to industrial applications, a slow gelation process means low productivity and is economically unfavourable.

The so-called fast or instantaneous gelation indicates that during the aggregation process, particles and clusters stick together at the very moment they touch, without subsequent internal rearrangements. Since the gelation rate is typically very fast, it is difficult to obtain a uniform gel by pouring the latex into a salt solution or *vice versa*. Thus, fast gelation is often carried out by dropping a given latex into a chosen salt solution under gentle agitation. The advantages of a fast gelation process are high productivity and the possibility of using continuous gelation units. This is therefore the method of choice in applications, although difficulties arise in controlling gel structure during the gelation process.

In order to investigate experimentally these processes, several types of pilot coagulators have been realized. One of them is constituted by a mechanically-agitated gelation reactor, where the latex is fed directly in the discharging region of the agitator blades. In this way, the mechanical agitation intensifies the dispersion of the latex in the solution, and in the meantime, the latex undergoes fast gelation. The objective is to understand the interaction between dispersion and fast gelation and to see the effect of the hydrodynamics on the gel structure. A typical result is shown in Fig. 6, where the specific gel volume (volume of gel per volume of latex) is given as a function of agitation speed for a latex with particle volume fraction of 0.07. It is seen that the specific gel volume increases as the stirring speed increases, which obviously indicates a variation of the gel structure with the stirring speed.

Received: January 15, 2001

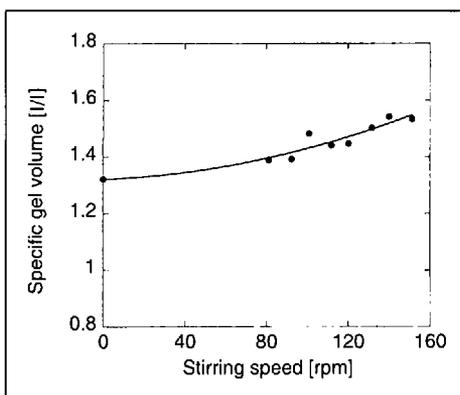


Fig. 6. Values of the specific gel volume (volume of gel per volume of latex) as a function of stirring speed for gelation of the fluorinated polymer, MFA[®] latex, with particle diameter of 75 nm and volume fraction of 0.07.

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