Scale-Up of Polymerization Process: A Practical Example

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Abstract:
The scale-up/-down of polymerization reactors has to deal with large viscosity changes during the process, addressing mass- and heat-transfer issues. A practical example on scale-up of styrene and methyl methacrylate free radical bulk and solution polymerization is presented. The main critical parameters are mixing at molecular level (micromixing) and heat removal capacity. The operating parameters being kept constant are: reaction conditions (temperature, pressure, chemistry) and thus the reaction time. A pilot plant issued from scale-down of possible industrial sizes was developed to represent, at best, larger scales. The main parameter being scaled-up is the heat removal capacity, which has to be maintained constant among the different sizes. New concepts are adapted to dissipate the mixing energy where it is the most suitable, and the final step is the scale-up/-down strategy. Another issue addressed in this contribution is the need for in-line analytics that could operate at different plant scales and thus give important information for process control. Scale-up/-down strategy must include the whole process, not only the reaction stage but also what happens before, after, and simultaneously, i.e., upstream, downstream, and peripheral operations. Finally the measurable success of a scale-up/-down analysis could only be proved at industrial scale, where a good agreement between pilot- and larger scale should be observed. The concepts in terms of transfer phenomena, analytics, separation, product properties, feasibility, and economics should also be included in this analysis.

Introduction

During the R&D of a chemical process, plant design requires special attention. Scale-up or scale-down procedures are part of the integrated process development. The challenge is to find the optimum between the chemistry, the design, the EHS (environment, hygiene, and safety) compliance, and economic factors. This iterative process requires concept discrimination at the early stage of the process development. A direct transfer from laboratory scale to the industrial scale is rarely feasible. Generally, one or several scales between the lab and the industrial process may be used. Thus, we have expressions such as bench scale, mini-pilot plant, pilot plant, quarter scale, half scale, demonstration unit, and so on that often vary from one company to another.[1]

A process development requires a good understanding of the chemical system in terms of kinetics, thermodynamics, hydrodynamics, and product properties. As the economic factor becomes more and more important, other aspects such as product quality, EHS, and productivity should not be forgotten.

Depending on the chemical reaction involved, the scale-up methodology should be adapted to the process characteristics. Often the process development is an iterative procedure combining scale-up and scale-down studies and trying to optimize factors such as: EHS, quality, process, design, control, costs, and constraints. Bulk and solution free radical polymerization will be used as an illustrative example.

Polymerization Reaction

Polymerization reactions can be classified as either step-growth or chain-growth reactions. It is important to note that this is a classification of reaction mechanisms, not of the repeating unit structure, since many polymers can be synthesized either by step-growth or chain-growth polymerization. Free radical polymerization belongs to the second class.

In chain-growth polymerization, polymer molecules generally grow to full size in a time-scale, which is much smaller than the time required for high conversion of monomer to polymer. The lifetime of a growing polymer molecule may be less than a few seconds for a free radical polymerization, which is a typical example of chain-growth polymerization, while a typical polymerization time to obtain high monomer conversion may be several minutes or hours such as that for the step-growth polymerization. Chain-growth polymerizations require an active center, which may be a free radical, cation, or anion. Once an active center is created, the polymer chain grows extremely rapidly, and when the growing chain is deactivated by a termination reaction, the polymer chain is "dead" and no longer takes part as a reactant. With free radical polymerization, however, the so-called dead polymer chain is not always truly dead, because under certain circumstances it may itself react with radicals. The active center may initiate the growth of several polymer chains.

For reactions evolving in complex media, most operating parameters change with time or size scale. In fact bulk or high solid content polymerizations start in water-like viscosity media (~1 mPa·s) ending in high viscosity range (10–1000 Pa·s). Hence, scale-up procedures are not trivial, and special attention has to be paid to this viscosity increase during polymerization, decreasing the heat- and mass-transfer rates. One has to describe correctly the transfer phenomena, the kinetics, and the media composition in evolving and rheologically complex fluids.

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(1) Euzen, J.-P.; Trambouze, P.; Wauquier, J.-P. *Scale-up Methodology for Chemical Processes*; Gulf Pub. Co.: Houston, TX, Paris, Éditions Technip, 1993.
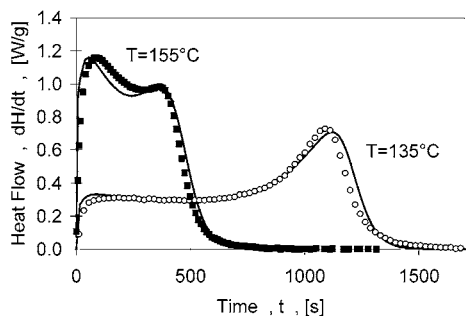
Figure 1. MMA polymerization modeling for two temperatures (initiator DTPB 50 mol·m^{-3}, 10% w/w ethyl benzene) [2]. Experimental value: dots; simulation: lines.

Figure 2. Examples of high-viscosity reactors.[4]

High solid content polymerization of methyl methacrylate (MMA) with free radical initiator is the chosen model system for the investigation of diffusion-controlled bimolecular termination and propagation and the decrease in initiator efficiency at high monomer conversions (cage effect). It has the largest Trommsdorff−Norrish effect because most of the polymer chains are produced by bimolecular termination and the higher-average molecular masses increase dramatically in the absence of a chain-transfer agent. The MMA polymerization reaction, measured by differential scanning calorimetry at two different temperatures and modeled according to Fleury et al. and Zeilmann,[2,3] is presented in Figure 1. The gel or Trommsdorff−Norrish effect (being accepted as a polymerization rate auto-acceleration) is clearly observable at 135 °C, starting after 250 s and being less present at 155 °C. The reaction time to complete the MMA polymerization is about 14 and 30 min at 155 and 135 °C, respectively. The correlation between the experiments and the model is really good, indicating that the parameters and the model describe well the observed measurements. This suggests that this model could be used for the scale-up/-down study. Therefore it is necessary to have a reliable kinetic model before accepting too many compromises that could lead to wrong development and expectations.

Polymerization Reactors

As the bulk- or solution-polymerization reaction evolves in high-viscosity media, special reactors could be used as presented in Figure 2. These kinds of reactors are generally suitable for high-viscosity processes, especially for polycondensation processes. Tubular-based loop reactors could be used instead for bulk or solution free radical polymerization.

A special reactor composed of a tubular loop reactor followed by a tubular part, all being completely filled with motionless mixers (Sulzer SMXL), was developed in collaboration with the manufacturer (Figure 3). The loop reactor can act as a continuous stirred tank as well as a plug flow reactor, depending on the recycle ratio used. This reactor concept was proved to be efficient for polymerization up to
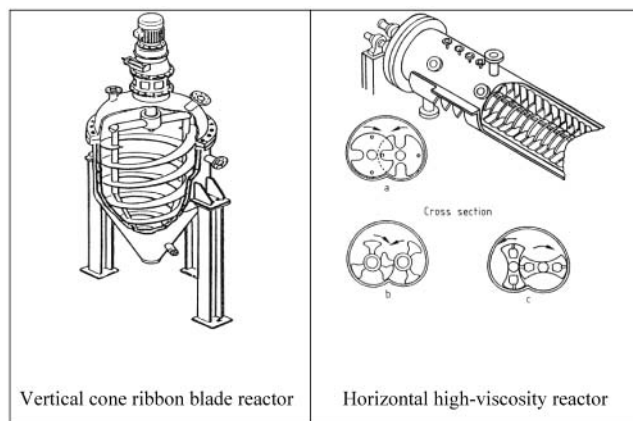
industrial scale. One of the major advantages is the reaction volume being less than that in classical stirred tank reactors and the control of temperature, which is greatly improved. The bulk/solution polymerization of styrene and methyl methacrylate were carried out continuously with remarkable product properties ($M_w \approx 150\,000$, $M_n \approx 90\,000$). The pilot reactor worked continuously for several weeks without plugging or fouling and delivered a constant product quality.

The pilot plant used in this work, with a maximum production capacity of 200 kg per day, is schematically depicted in Figure 3. This pilot installation consists mainly of four parts indicated with the letters A−D. It consists of a tubular loop reactor (A) followed by a plug flow reactor (pptube). The preheating (B) and devolatilization (C) parts guarantee the continuous separation of polymer from volatiles for the production of low-residual-content polymer. The monomer-feed stage (D) ensures a controlled composition and monomer feed into the reactor.

Polymerization Modeling

Since 1980, modeling of polymerization reactors has become more comprehensive. To develop a predictive model, account must be taken of the chemistry and physics of all the microscopic processes that occur in the polymerization process.[5] The polymer reactor model is now becoming accepted as a valuable tool whose use contributes significantly to all aspects of process technology for polymer manufacture. This includes process design, optimization, state estimation, and control. Polymers with a unique and desirable combination of properties can often be obtained through process design. Process parameters such as residence time distribution (RTD) are usually not considered by polymer synthesis chemists, although RTD can influence chemical composition distribution, molecular mass distribution, long-chain branching, and gel/sol ratios. In the early days of the polymer industry, the chemist played the major role in product and process development and scale-up. This has changed, with the process engineer now playing a significant role in all phases of commercialization of new and improved polymer products. His broad experience with process fun-

(2) Fleury, P.-A.; Meyer, Th.; Renken, A. In *4th International Workshop on Polymer Reaction Engineering*; Kreysa, G., Reichert, K.-H., Eds.; VCH: Weinheim, 1992; Vol. 127, p 31.
(3) Zeilmann, T. Continuous methymethacrylate polymerization process, Swiss Federal Institute of Technology (EPFL), No. 2554, 2002.
(4) *Ullman's Encyclopedia of Industrial Chemistry*; VCH: Weinheim, 1992.
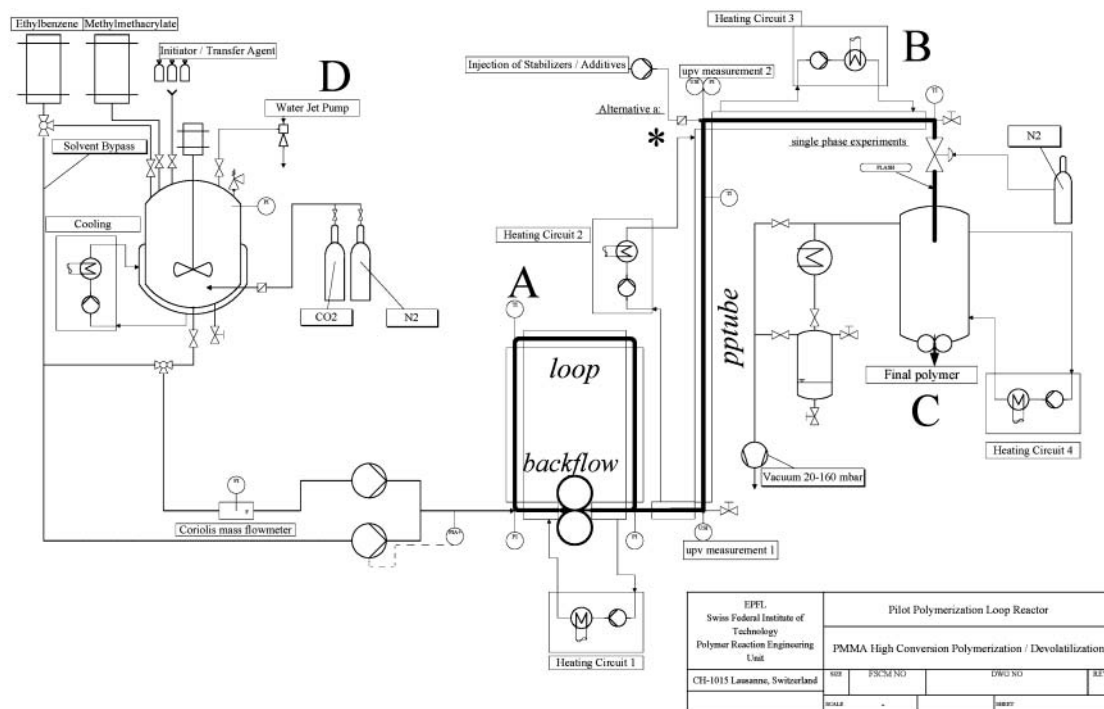(5) Wilks, E. S. *Industrial Polymers Handbook*; Wiley-VCH: Weinheim, 2001.
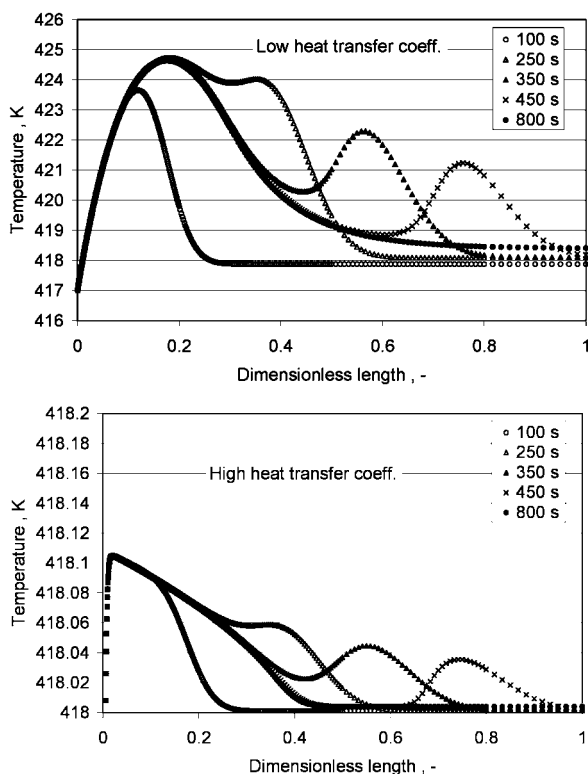
Figure 3. Polymerization pilot plant.

Figure 4. Dynamic temperature profile in a tubular reactor for a MMA solution polymerization (12% solvent mass fraction, T_{wall}: 418 K, T_{inlet}: 417 K, $C_{initiator}$: 50 mol/m^3) [3].

damentals and computer modeling is essential to obtain high-quality products, safely, respecting EHS constraints, and in an economic manner.[4]

Dynamic reactor models can be used in a variety of ways. An example is given (Figure 4) for the MMA polymerization by dynamic modeling in tubular reactor, showing the effect of heat-transfer coefficient on the temperature profile. It can
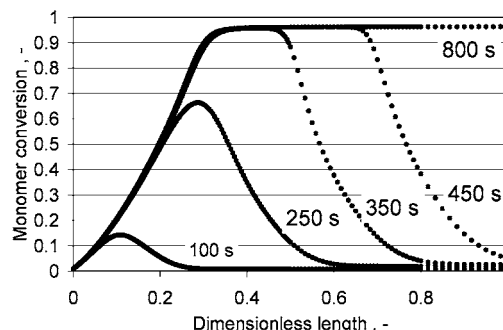

Figure 5. Dynamic monomer conversion profile for a MMA polymerization at 145 °C [3], same conditions as for Figure 4.
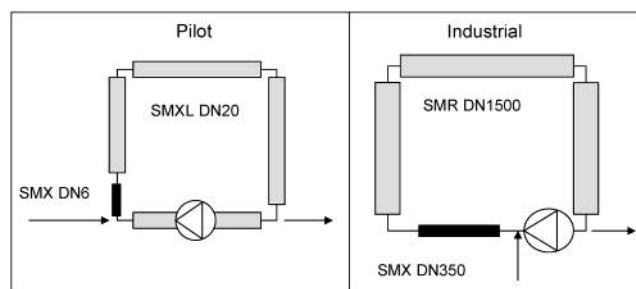

Figure 6. Scale-up of intensive mixing zone in loop reactors.

be observed that depending on the heat removal capacity, the temperature profile is strongly different going from a hot-spot presence to a quasi-isothermal polymerization. The corresponding monomer conversion profile is presented in Figure 5 where the strong gel effect is observable since 20% conversion. Stability and control of polymer reactors should be considered at the design stage and control problems minimized then, rather than corrective action taken after the plant is built. Complex interactions which are involved in polymerization (highly nonlinear temperature and concentra-
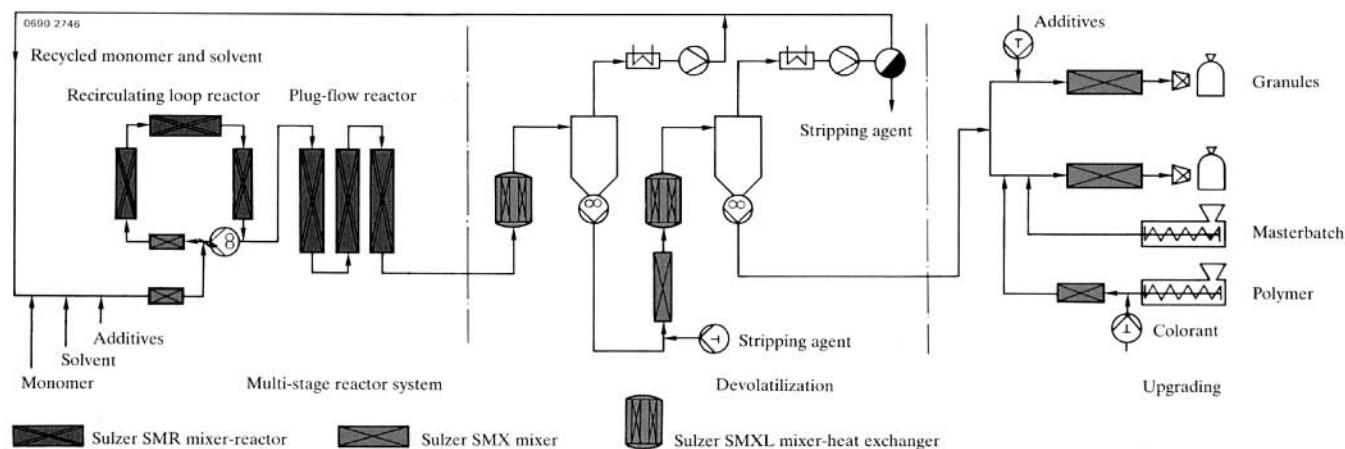
Figure 7. Schematic drawing of an industrial polystyrene plant, copyright Sulzer,[9] reprinted with permission.

tion effects) preclude optimal design based on experimentation alone because the cost would be prohibitive. Models can be used to identify potential sources of product variability and strategies to minimize their effects. Models can also be used to store information on process technology in a concise and readily retrievable and modifiable form.

Process models can be used to train chemists, chemical engineers, and plant operators and give them an awareness of the dynamics of the polymerization process. The most expensive aspect of model development is experimental estimation of model parameters; highly instrumented bench-, pilot-scale, and plant-scale reactors are required. Statistically designed experiments should be performed to permit efficient parameter estimation and model development. Modeling is an iterative process, and the very act of developing a deterministic model permits a greater understanding of the relevant microscopic processes which occur during polymerization or polymer modification. As additional data (plant, pilot-plant, and bench-scale) become available, model structure and parameters can be updated.

Scale-Up Aspects of Polymerizations

Very little publicly available information could be found on the scale-up of polymerization reaction and processes.[6] Several questions have to be answered during the scale-up/-down process, such as: What should be kept constant in the process? Which factors should be scaled-up/-down? What are the important parameters? Which design concept is better? What will the process control strategies be? Is the process EHS-compliant?

To focus on crucial parameters in scale-up studies, it is important to define what has to be kept constant. In the case of solution and bulk polymerization, reaction time, heat removal capacity, and the degree of homogeneity should be kept constant. To maintain constant reaction time means that operating parameters such as chemical composition, temperature, pressure, and mixing quality must also be kept constant. Assuming that the chemical recipe is identical, one has to concentrate on heat- and mass-transfer aspects.

Before there is any scale-up/-down design, one has to evaluate the following: Where are the limitations are? How can they be faced? And what are the consequences? In the

case of loop reactors, special attention has to be paid to the degree of mixing (a better understanding of the degree of mixing in high-viscosity media is of crucial interest with regard to the product quality during a polymerization reaction), energy dissipation, heat transfer, and required heat capacity removal ($\sim$1 MW/m^3).

Sulzer static mixers were used in our polymerization pilot plant. The choice, among several types (Kenics, Koch, and so forth), without including an economic factor at this stage of process development, was imposed by the need of high micromixing efficiency and heat transfer on one hand and by the scale-up possibilities on the other hand. Other mixer types could be used when heat capacity removal is lower or when mixing is not the critical issue.

Concerning mass-transfer phenomena, micromixing aspects should be taken into consideration. The reactor design could also be improved to dissipate the mixing energy at locations where intensive mixing is required (in our case one location is situated at the monomer inlet feed). This concept should be feasible in scale-up/-down procedures. In loop reactors it is possible to dissipate 80−90% of the total mechanical energy (achieved by Sulzer SMX-type mixer) only in the zone where intensive mixing is required [7,8] (mixing of low-viscosity fluid, i.e., a monomer mixed with the high-viscosity reactive polymer solution) as presented in Figure 6 at pilot and industrial scale (dark zone = intensive mixing). The remainder of the dissipated energy used in the rest of the reactor maintains mixing and heat transfer. This concept is the result of the scale-up study that could be applied either at pilot or industrial scale, enforcing the scale-up/-down compatibility.

The heat transfer or more precisely, the heat-transfer coefficient per volume unit should be kept constant among the pilot and the industrial scale. Two different types of static mixers have to be employed to fulfill the above-mentioned requirements. At industrial scale the Sulzer SMR mixer could afford a global heat-transfer coefficient of 26 kW·m^{-3}·K^{-1}

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(6) Meyer, Th. *Curr. Opin. Drug Discovery Dev.* **2002**, *5*, 960.
(7) Meyer, T.; Renken, A. In *Proceedings of the Third Berlin International Workshop on Polymer Reaction Engineering*; Reichert, K.-H., Geiseler, W., Eds.; VCH: Weinheim, 1988; p 285.
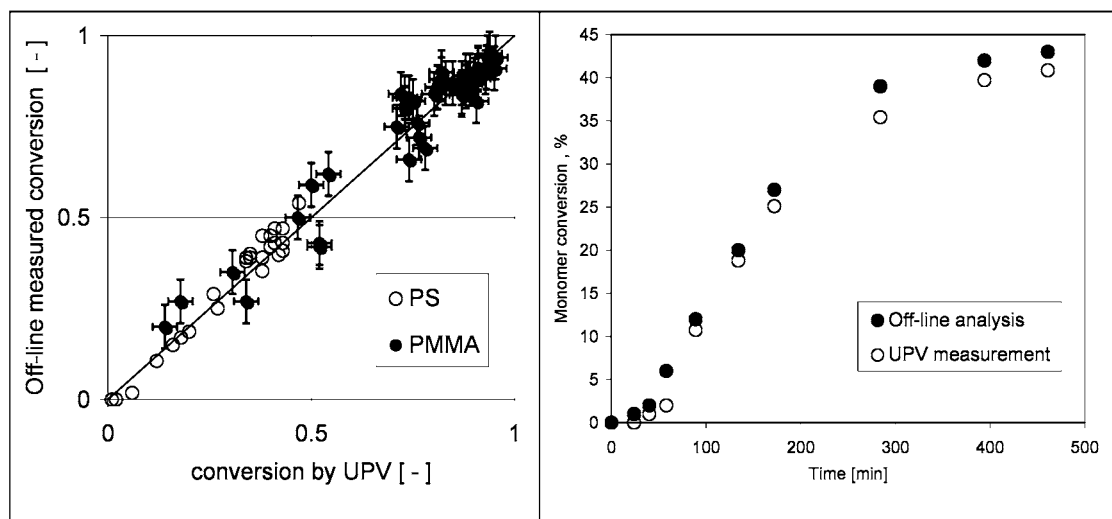(8) Meyer, T.; Renken, A. *Chem. Eng. Sci.* **1990**, *45*, 2793.

Figure 8. Parity plot for off-line (sampling and gas chromatography analysis) and in-line measurements (UPV).
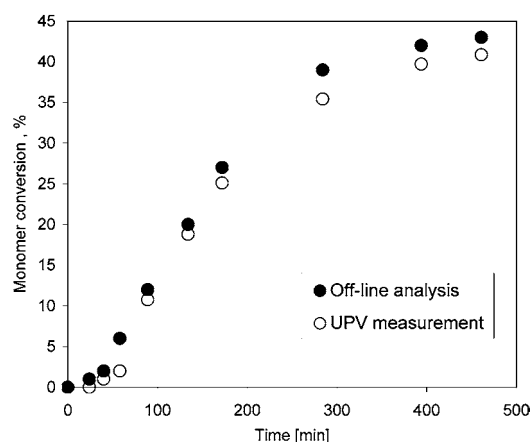

Figure 9. MMA monomer conversion evolution in the dynamic state.

Figure 10. Scale-up/-down of UPV in-line control.

from the size DN100 to DN1500. The scale-down procedure will indicate the suitable size of SMXL mixers that corresponds to the same coefficient. The result is that a SMXL DN 20 will give a global heat-transfer coefficient of 28 kW·m^{-3}·K^{-1}. The pilot-scale reactor must be constructed at this size; other configurations will lead to a nonrepresentative pilot–industrial scale-up/-down procedure.

The industrial-size plant drawing is presented in Figure 7, where the abovementioned scale-up/-down results are integrated for the mass- and heat transfer.

Scale-Up Strategy Applied to In-Line Control

Once a process has been correctly described, an adequate strategy for process control has to be established in terms of reactor behavior and product quality by the means of sensors, models and processes. The useful operating measurements (temperature, pressure, flow rate, monomer conversion, and viscosity) have to be scale-up/-down compliant. This seems trivial for temperature and pressure but could be difficult for viscosity, conversion, and product properties. The application of the UPV (ultrasound propagation velocity) technique to follow the media composition evolution during
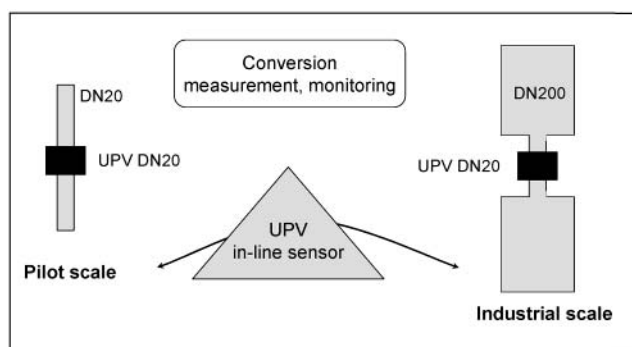
the polymerization reaction in the reactor was developed.[10−12] The sensors can be directly inserted into the tubular reactor (Figure 3) and do not require a sampling circuit. This allows in-line monitoring of the instantaneous monomer conversion in high-viscosity media as presented in Figures 8 and 9 for the styrene and MMA polymerization. It could also be adapted to pilot scale as well as industrial scale as presented in Figure 10. The same approach used in pilot scale could be applied to larger scale without the need of tedious scale-up studies and technical developments.

Conclusions

The choice of the right scale for the pilot plant is of crucial relevance towards the industrial size to be addressed. The main parameters as well as the kinetics, thermodynamics, and technologies should be clearly defined. For the studied polymerization system, reaction parameters such as chemistry, temperatures, pressures, and reaction time were kept constant among the scale-up process. All the efforts were concentrated on heat- and mass transfer, these being defined as crucial parameters. The limiting factors such as mixing efficiency and heat-removal capacity were addressed to be comparable at pilot and industrial scale. The scale-up process

(9) Sulzer-Chemtech, AG. Misch- und Reaktionstechnik; No. 23.27.06.20-X.94-100.
(10) Cavin, L.; Meyer, Th.; Renken, A. *Polym. React. Eng.* **2000**, *8*, 201.
(11) Cavin, L.; Renken, A.; Meyer, Th. *Polym. React. Eng.* **2000**, *8*, 225.
(12) Zeilmann, T.; Lavanchy, F.; Meyer, Th. *Chimia* **2001**, *55*, 249.

was an iteration between scale-up and scale-down. It has been demonstrated that not every pilot scale is the right industrial scaled-down size.

The scale-up process should play an important role in the design procedure. Special attention has to be paid to the technical limitations and when possible take advantage of scale-up similitude as it was the case with static mixers being totally different at both scales (Sulzer SMXL for pilot and Sulzer SMR for industrial size). Control and measurements, especially in- or on-line ones, should be associated with scale-up/-down procedures. In- or on-line sensors are preferred and assessed in the scale-up feasibility.

Scale-up/-down studies are part of the iterative process development and should be closely integrated in a multidisciplinary approach encompassing several branches of science and engineering. All the concepts being developed should be employed at pilot scale as well as industrial size. The scale-up studies should be able to predict the reactor behavior from pilot plant to full scale.