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Polymer Reaction Engineering at EPFL

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Abstract: The polymer reaction engineering group at EPFL takes an active part in the following research fields:
Reaction engineering:
- Kinetic modeling of polymerization reactions (lab and pilot scale reactors), free radical, polyepoxydation, polycondensation.
- Development, scale-up and optimization of continuous polymerization processes.
- Development of inline analytical sensors for polymerization process control.

Polymerization reactions:
- Polymerization initiated by multifunctional initiators.
- Polymerization under supercritical conditions.
- Development of selective adsorbents from modified polymers.

Several topics such as inline sensors, multifunctional initiators, polyepoxydation and modification of polymer matrices are presented.

Keywords: Kinetics · Modeling · Polymer · Reaction Engineering

1. Introduction

The polymer reaction engineering group (PRE) is part of Chemical Reaction Engineering in the Chemistry Department (DC-LGRC) at the Swiss Federal Institute of Technology in Lausanne. Research is focused on polymers and polymerization reactions at lab and pilot scale. One key research area is the fundamental description of polymerization kinetics with high solid contents under unusual reaction conditions such as highly viscous systems or supercritical media. Polymerization process optimization as well as performance and product quality improvement can be efficiently realized only with a strong understanding of polymerization kinetics, transfer phenomena and with adequate reactor behavior modeling. A second key topic is the development of new inline sensors for polymerization reaction control. New concepts using ultrasonic technologies are used for inline monomer conversion measurements and pilot reactor monitoring. The last research field is concerned with the development of quantitative and selective radionuclei adsorbents based on modified polymer matrices. Some of the ongoing research is presented.

2. Inline Sensors

Online conversion measurements in chemical reactions are essential for process monitoring and control. In order to obtain this information a new tool, based on ultrasound propagation measurements, for inline monitoring of polymerization reactions has been characterized. The ultrasonic propagation velocity (UPV) depends on adiabatic density and compressibility in gases, liquids or solids [1][2] :

$$c^2 = \frac{1}{\bar{\rho}\bar{\beta}} \tag{1}$$

Where c is the ultrasonic propagation velocity and $\bar{\rho}$ the mean density and $\bar{\beta}$ the mean adiabatic compressibility.

In the case of polymerization reactions, as the monomer conversion increases, density and compressibility of the polymeric system change. Therefore by measuring UPV, the temperature and pressure near the probe, monomer conversion can be estimated. Using the additivity rule [3][4] and mass fraction, a direct relation between ultrasonic propagation velocity and polymer mass fraction w_p is obtained (p: polymer, m: monomer, s: solvent) :

$$\frac{\sum_i \frac{w_i}{\rho_i}}{c - \alpha P} = \sqrt{\left(\frac{w_p\beta_p}{\rho_p} + \frac{w_m\beta_m}{\rho_m} + \frac{w_s\beta_s}{\rho_s}\right)} \tag{2}$$

The ultrasonic sensor, directly inserted in the reactor, does not require a sampling circuit and its use is particularly simple and suitable for laboratory and industrial purposes. Inline measurements (UPV method) are in good agreement with the results obtained by offline headspace gas chromatography, at low as at high monomer conversion and solid content.

This technique allows not only the determination of the solution composition evolution during the polymerization but also the residence time distribution, opening the way to online reactor control and reaction monitoring without any sampling and tedious analysis [2][5][6] (Fig. 1).

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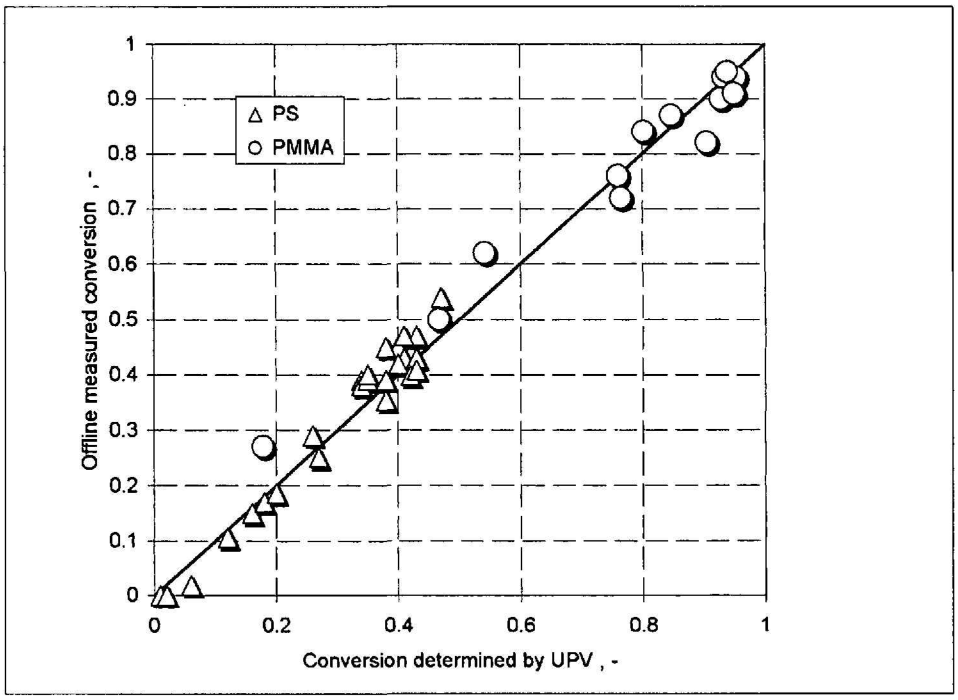


Fig. 1. Comparison between offline analysis and inline UPV measurements [2][6].

3. Multifunctional Initiators

Due to the nature of free radical polymerization, it is not possible to obtain high polymerization rates and simultaneously a high molecular weight in bulk or solution processes. The problem can be overcome by using multifunctional initiators and by controlling the decomposition rate of the labile groups [7]. The presence of a second radical generating function distributed in the growing and dead polymer can be engaged in further initiation, propagation, chain transfer and termination reaction during the course of polymerization. Thus, bifunctional initiators appear to be a new alternative to control efficiently the molecular weight and monomer conversion. However, the presence of these additional functional groups leads to complex polymerization kinetics. Generally, there are two families of bifunctional initiators: the symmetrical one with two identical labile groups having the same thermal stability and the unsymmetrical one having labile groups with different thermal stabilities. Studies on batch bulk polymerization of styrene initiated with symmetrical [8–11], with unsymmetrical [12], with a mixture of symmetrical [13] and even recently with a mixture of mono and bifunctional initiator have been performed [14]. The interest of such investigations is the development of kinetic models allowing the description of experimental results and optimization of new polymerization routes.

There is also an interest in using polyfunctional initiators to produce polymers of tuned properties. Kim and Choi [15] analyzed the steady state behavior of a CSTR for the bulk polymerization of styrene initiated with a symmetrical bifunctional initiator. Yoon and Choi [16] studied the free radical solution polymerization of styrene initiated with a binary mixture of symmetrical bifunctional initiators in a tubular reactor filled with static mixers. A dynamic axial dispersion model is used to investigate the transient behavior of the reactor.

In order to use efficiently initiators during the styrene polymerization in a continuous reactor, it is necessary to propose a kinetic model and to validate it by experimental measurements. The concentration evolution of each species is obtained by numerical integration of differential moment equations. The k-order moment of one species in solution is defined as follows [17]:

$$\lambda_{\xi,k}=\sum_{n=j}^{\infty} n^k \xi_n \qquad (3)$$

$\xi=P, Q, S, U, Z$ or M'
$j=1$ for P, Q, S, Z
and $j=2$ for M', U

$\lambda_{\xi k}$ is the k order moment of the species ξ. For instance, the 0 order moment represents the overall concentration of one species, every length mixed up. It is simply denoted ξ_t. The concentration of R, R' and R_A are calculated with the quasi steady state assumption (QSSA):

$$R_A=\frac{2f k_d I}{k_d+k_t M} \qquad (4)$$

$$R'=\frac{f k_d R_A}{2k_t M}$$

$$R=\frac{f k_d}{k_t M}(2I+R_A+Q_t+2U_t+Z_t)$$

The volume can be expressed as a function of monomer conversion and volume contraction factor ε:

$$\varepsilon=\frac{V_{X=1}-V_{X=0}}{V_{X=0}} \qquad (5)$$

$$V=V_0(1+\varepsilon X) \qquad \frac{dV}{dt}=V_0\,\varepsilon\frac{dX}{dt} \quad (6)$$

The concentration variation of the initiator, monomer, as well as the 0, 1 and 2 order moment of each species are calculated from the reaction rate and volume variation:

$$\frac{dE}{dt}=R_E-E\frac{dV}{Vdt} \qquad E=\lambda_{x,\xi}\ I,\ M \quad (7)$$

A comparison of reaction rate in terms of heat release, between experimental data and simulations are reported in Fig. 2. The model is in good agreement with experiments and shows that there is a strong tendency to enter the gel effect above a monomer conversion of 60%.

4. Polyepoxydations

Solid epoxy resins are used in surface coatings and adhesives. They are produced by mixing bisphenol A (BPA) with low-molecular weight liquid resins (RBL) which contain epoxy groups. These polymerization reactions are catalyzed. The principal reaction of epoxy groups with phenolic hydroxyl functions leads to linear polymer chains formation (advancement reaction). Secondary hydroxide functions can further react with epoxy groups and these branching reactions increase molecular weight and viscosity, and therefore control the product commercial specifications (Scheme).

Kinetic studies have shown that alkoxide ion reacts faster with phenolic hydroxyl groups due to its higher nucleophilic properties and advancement reaction is favored. At the end of the linear reaction, branching reaction continues and allows the final viscosity control.

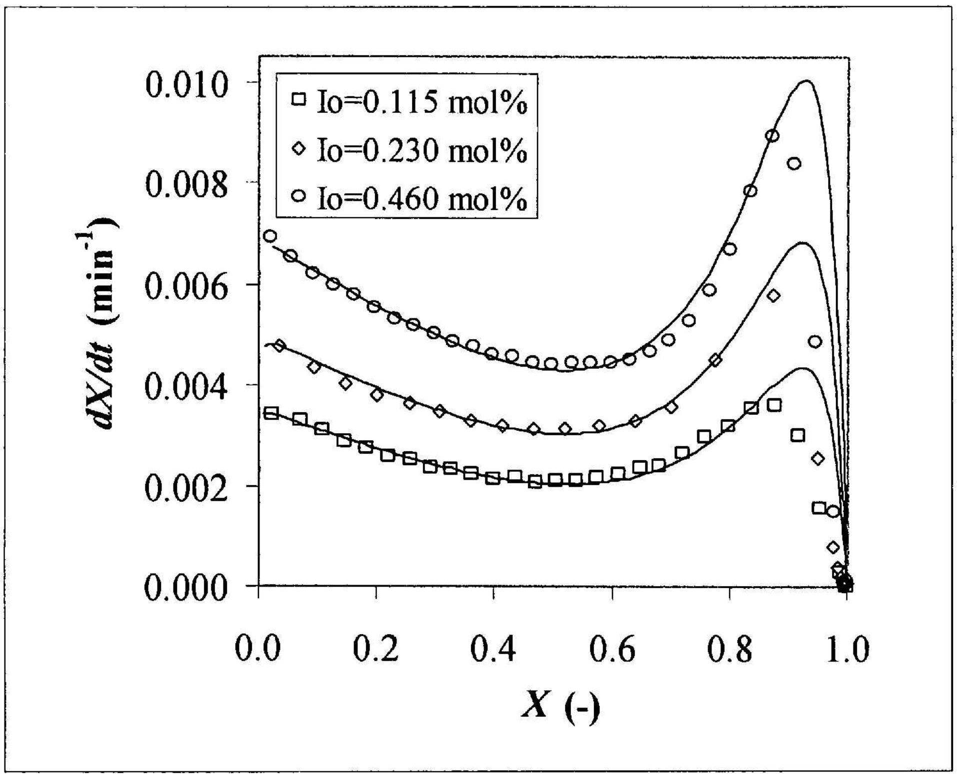
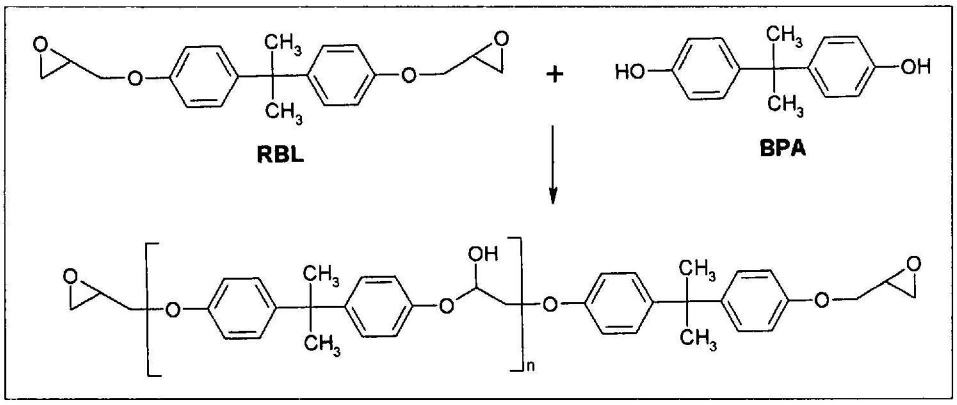


Fig. 2. Evolution of the reaction rate and conversion for the bulk free radical styrene polymerization initiated with Lu256 at 80 °C.



Scheme

The kinetic model takes into account both advancement reaction and branching reactions. Using diffusion model and Stokes-Einstein rule, Eqn (8) and (9) are obtained:

$$-\frac{dC_{Ep}}{dt} = k_{ad,\infty}\exp\left(\frac{-E_{ad}}{RT}\right) C_{cat} C_{Ep} C^{n}_{OHp} + \frac{k_{br,\infty} T}{T + k_{br,\infty} K_{diff} C_{Ep} \eta_{red}} \exp\left(\frac{-E_{br}}{RT}\right) C_{Ep} C_{OHs} \quad (8)$$

$$-\frac{dC_{OHp}}{dt} = k_{ad,\infty}\exp\left(\frac{-E_{ad}}{RT}\right) C_{cat} C_{Ep} C^{n}_{OHp} \quad (9)$$

This model describes experimental results at lab (reactor volume 2 liters) and industrial scale reactors (reactor volume 16 m^3) as shown in Fig. 3. It is used for scale-up and optimization of a new continuous process.

5. Modification of Polymer Matrices

Due to mining, processing and industrial use, natural radionuclides can be mobilized and may contaminate surface and ground waters. They also can be present in drinking waters at non-acceptable levels as a consequence of natural leaching processes. Wastewaters from nuclear fuel processing plants are also a very important source for environmental contamination by transuranic nuclides.

The introduction of new European laws (2000) and WHO recommendations set very restrictive radionuclide concentrations in drinking water. These regulations require a large increase of radioactive survey programs. Actually the cost and high technicality of existing analytical technologies and procedures are not able to fulfill such needs. In order to provide a solution to this problem, the project RADIOSAF was started in 1999. The principle of radionuclides detection is based on the selective adsorption of transmitting radionuclides by very thin modified polymer matrices (Fig. 4). A small disk of the adsorbing material is simply placed into a small bottle containing to water to be analyzed. After adsorption, the radionuclide present on the disk is analyzed with a small alpha particles detector. The main objective is to develop modified polymer matrices able to adsorb radionuclides with a high selectivity. The system is able to detect alpha activity in the range of 1 mBq/l to 10Bq/l.

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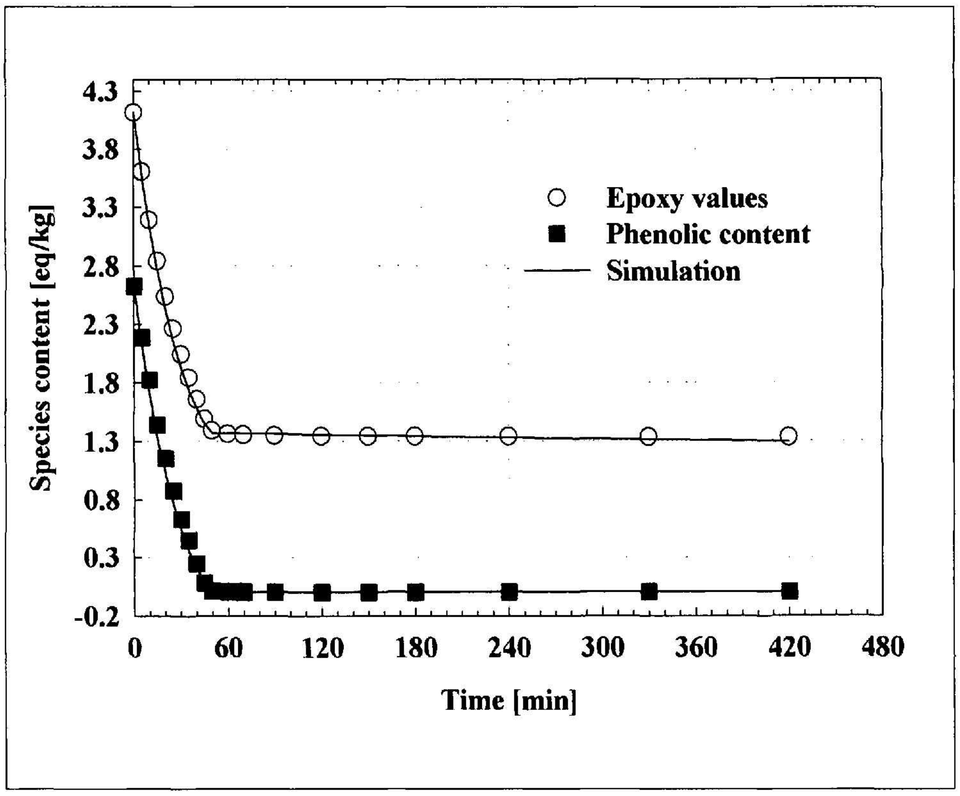

Fig. 3. Model validation for the polyepoxydation reaction.

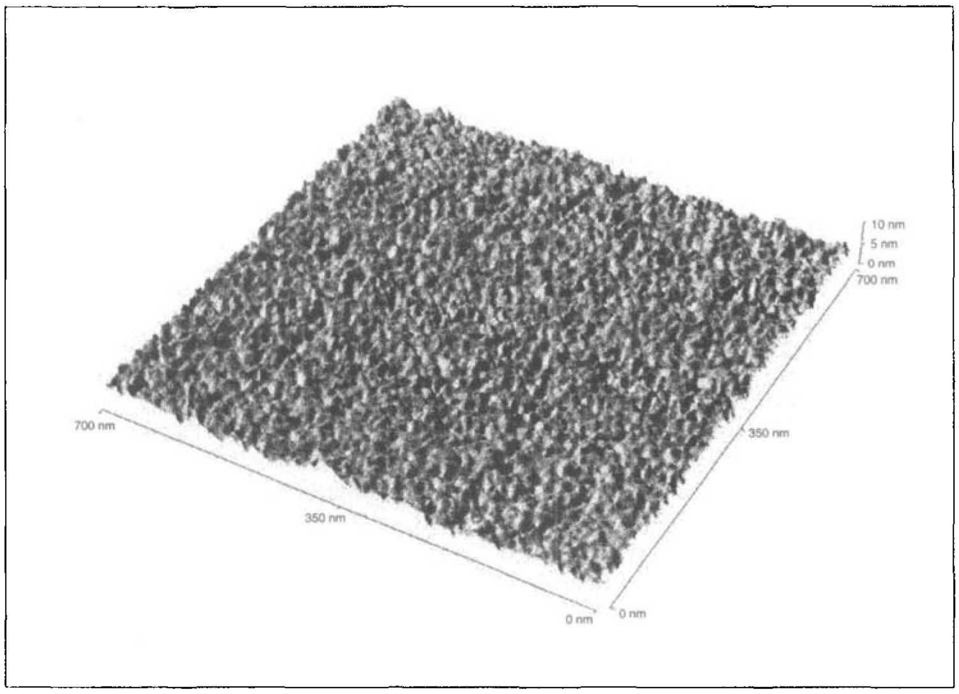

Fig. 4. Atomic force microscopy of the adsorbing media.

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