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COMPARISON OF TECHNIQUES FOR THE DETERMINATION OF CONVERSION DURING SUSPENSION POLYMERIZATION REACTIONS

J. C. Santos[1], C. N. Lopes[1], M. M. Reis[2], R. Giudici[3], C. Sayer[1],
R. A. F. Machado[1] and P. H. H. Araújo[1,*]

[1]Universidade Federal de Santa Catarina, CTC, Departamento de Engenharia Química e Alimentos,
Phone: (48) 3721-9448, Fax: (48) 3721-9687,Cx P 476, CEP: 88040-970, Florianópolis - SC, Brasil.
E-mail: pedro@enq.ufsc.br
[2]Fundação Universidade Federal de Rondônia, UNIR, Campus-BR 364,
Km 9.5, CEP: 78900-000, Porto Velho - RO, Rondônia, Brasil.
E-mail: marlon@unir.br
[3]Universidade de São Paulo, Escola Politécnica, Departamento de Engenharia Química,
Phone: (11) 3091-2246, Fax: (11) 3813-2380, Cx. P. 61548,
CEP: 05424-970, São Paulo - SP, Brasil.
E-mail: rgiudici@usp.br

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Abstract - The determination of conversion during suspension polymerization reactions is not an easy task due to the heterogeneity of the reaction medium and the tendency of particles to agglomerate rapidly when stirring is stopped. Usually, bulk polymerization in ampoules is employed to study the kinetics of suspension polymerization reactions. In this work, a comparison of different techniques for the determination of conversion during suspension polymerization reactions is presented. Results showed a good agreement between the conversion obtained by gravimetry during styrene suspension polymerization and on-line conversion monitoring data using fiber-optic based Raman Spectroscopy. Nevertheless, the polymerization rate of styrene bulk polymerization carried out in ampoules was higher than the real reaction rate of styrene suspension polymerization due to slightly higher reaction temperatures. Simulation results using the experimental temperature data in a mathematical model confirmed these results.

Keywords: Suspension polymerization; Bulk polymerization; Gravimetry; Styrene; Raman spectroscopy.

INTRODUCTION

Suspension polymerization is a reaction, via free radicals, that occurs in a heterogeneous medium. In a typical suspension polymerization system, one or more monomers relatively insoluble in water and initiators soluble in oil (the initiation reaction takes place in the organic phase), are dispersed in the continuous aqueous phase by the combination of a strong stirring and the use of small amounts of suspension agents (stabilizers). As long as the stirring is maintained, the monomer droplets are slowly converted from a highly mobile liquid state into a viscous dispersion (conversion between 20 to 60%), and then into solid polymer particles (conversion > 70%) (Yuan et al., 1991). The initial size distribution of monomer droplets does not remain equal to the final polymer particle size distribution, because the monomer droplets/polymer particles suffer a continuous process of coalescence and breakage. According to Alvarez et al. (1991), these coalescence and breakage kinetics are deeply influenced by the particles' rheology, which in turn is affected by the reaction kinetics, since the progress

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*To whom correspondence should be addressed of the reaction makes the particles more and more viscous. Therefore, the knowledge of suspension polymerization reaction kinetics is very important, not only for reaction rate control, but also for control of the final particle size distribution (Machado et al., 2000).

The usual particle size of a suspension polymerization for the production of rigid foams (e.g., expanded polystyrene) ranges between 500-1200 μm (Klodt and Gougeon, 2003). Since these particles are not stable, when stirring is stopped, they tend to agglomerate rapidly and to separate from the aqueous phase, due to density differences. These factors make it difficult to collect samples that are representative of the reaction media of a suspension polymerization reactor. Even in a laboratory scale reactor it is necessary to collect a relatively large sample aliquot (5-10 ml per sample) in order to guarantee that it is representative. Besides that, the operation must be fast to avoid the influence of rapid particle agglomeration and phase separation on the measurement.

A technique proposed by Bishop (1971) was used by Santos et al. (1998) to determine the conversion during a styrene suspension polymerization reaction. In this technique, a 10 ml sample is taken from the reactor and placed in a glass beaker containing hydroquinone (inhibitor). This beaker is then placed in a box with ice to quickly cool down the sample. Afterwards, the beaker is weighed and the sample is placed in a vacuum oven at 40º C, so that the volatile components (water and residual monomer) evaporate, until a constant weight is achieved. Nevertheless, this technique presents results that are only satisfactory, as can be seen in the work of Santos et al. (2000).

It is commonly accepted that suspension polymerization reaction kinetics are similar to bulk polymerization kinetics where each drop of monomer/polymer particle behaves as a mini bulk reactor (Vivaldo-Lima et al., 1997). Since the determination of the evolution of conversion in suspension polymerization reactions is not an easy task and results are only satisfactory, several works have used bulk polymerization in ampoules to study the kinetics of suspension polymerization reactions (Vivaldo-Lima et al., 1997). On the other hand, it is not possible to state categorically that a specific suspension polymerization reaction follows the same conversion profile that was determined for a bulk polymerization. For instance, it has been observed that, for systems that present a very pronounced gel effect, as methyl methacrylate (MMA) polymerizations, the reactions carried out in ampoules of 5 mm o.d. (or larger) result in higher polymerization rates due to non-homogeneous thermal effects (Zhu and Hamielec, 1991). Besides thermal effects, other factors, such as contamination by inhibitor, etc, may influence the reaction rate. Therefore, only by tracking the conversion of a suspension reaction is it possible to obtain the exact rate of this reaction.

According to Kiparissides and Morris (1996), many of the problems found in the control of polymerization reactions can be attributed to the lack of analytical instruments and sensors able to provide on-line measurements during the reaction progress. In suspension polymerizations, the techniques are usually more complicated due to the heterogeneity and viscous nature of the polymerization media, which can make representative sampling more difficult. Only a relatively small number of works involve the monitoring of suspension polymerization reactions; these works use different monitoring techniques such as ultrasound (Sladky et al., 1979; Henning et al., 2000), calorimetry (Maschio et al., 1999), NIR spectroscopy (Santos et al., 1998) and Raman spectroscopy (Hergeth et al., 2003; Santos et al., 2004).

Free radical styrene polymerization does not present a gel effect (autoacceleration) as pronounced as MMA polymerization systems. However, when a crosslinker like divinylbenzene (DVB) is added to styrene (S), the temperature rise in S-DVB copolymerization reactions carried out in ampoules could be significant as the gel effect is stronger for higher amounts of crosslinker (Sajjadi et al., 1996; Vivaldo-Lima et al., 1998). In this work, a comparison of different techniques for the determination of conversion during styrene suspension polymerization reactions is presented. Gravimetric data obtained during the suspension homopolymerization reaction were compared with those of a bulk homopolymerization in ampoules. For on-line conversion monitoring of styrene suspension polymerization, the technique of Raman spectroscopy was employed. Finally, simulations with a mathematical model were performed to confirm experimental results.

EXPERIMENTAL PART

Reagents

Styrene, with a purity degree higher than 99.6% and a p-tert-Butyl Catechol inhibitor concentration of 12 ppm, was supplied by Inova. Benzoyl peroxide, BPO, (75% of active oxygen, half life time of one hour at 92ºC) supplied by Elf Atochem Chemicals in p.a. quality was used as initiator. Polyvinylpyrrolidone, PVP, K-90 with a weight average molecular weight of 360000 g/gmol, supplied by ISP Technologies INC was used as stabilizing agent. Dodecylbenzene sulfonic acid sodium salt (DBSS) and p-benzoquinone, both from Sigma-Aldrich Chemie, were employed, respectively, as surfactant and inhibitor. Distilled water was used as continuous phase. Toluene, p.a. quality (brand Nuclear), was used to dissolve the organic phase. All the reagents were employed as received.

Suspension Polymerization Reactions

For the suspension polymerization reactions, the initial charge (water and styrene) was purged with nitrogen during 60 minutes, and the nitrogen feed to the reactor was maintained during the reaction to avoid inhibition by oxygen. PVP and DBSS were added during the polymerization process. (see Table 1).

a) Gravimetry

The conventional procedure applied in the gravimetric measurements for suspension polymerization reactions, as proposed by Bishop (1971), presents only satisfactory results. One of the reasons for this could be the relatively long time required to interrupt the reaction. In the conventional procedure, the samples are cooled before being weighed. Nevertheless the time necessary to cool down effectively the polymer particles can vary significantly accordingly to the amount of sample collected, the time required to place the beaker in ice, etc. This variation influences not only the real polymerization rate, since the conversion is not stopped instantaneously, but also allows part of the monomer contained in the particles to be lost by evaporation before the beaker is weighed. The use of an aqueous solution of hydroquinone as inhibitor can also lead to a certain inefficiency when stopping the reaction because, even though hydroquinone is soluble in the organic phase, it is also very soluble in the aqueous phase, which is the continuous phase of the suspension polymerization. Besides that, even during the intermediate polymerization stages (above 40% conversion) the viscosity of the polymer phase is quite high, which results in limitations of the diffusion of the inhibitor inside the polymer particles, where the initiator is located and the reaction occurs.

In this work, another procedure was employed for the gravimetric measurements. In this procedure a sample, approximately 5 g of the suspension, is taken from the reactor. This sample is placed in an aluminum capsule and weighed immediately. In order to guarantee that the reaction is instantaneously stopped, right after weighing the sample, 5 g of toluene containing 0.05 g of p-benzoquinone inhibitor, that is soluble only in the organic phase, are added to the capsule. Since polystyrene is very soluble in toluene, the polystyrene particles are rapidly swollen and dissolve in it. In this manner, the inhibitor contained in the toluene is able to react immediately with the remaining radicals, guaranteeing that the reaction is interrupted. After the addition of toluene with inhibitor, the sample is dried in a vacuum oven until constant weight is reached. At the end, the dry mass is weighed and the polymer conversion is determined. This gravimetric technique was employed in this work to obtain the conversion evolution during the suspension polymerization reactions.

b) Raman Monitoring

In order to track on-line the evolution of conversion during suspension polymerization reactions, Raman spectra were collected in a FRA 106/S FT-Raman accessory coupled to a Bruker IFS 28/N spectrometer, equipped with a quartz beamsplitter. The spectral range comprises equally spaced measurements from 100 to 4000 cm^{-1} with a resolution of 8 cm^{-1} and the laser wavelength and power were 1064 nm and 450 mW, respectively. During styrene suspension polymerization reactions, spectra were collected with 32 scans, to allow fast measurements compatible with the batch reaction dynamics, and the Raman probe was connected to the 15 mm glass window of the reactor as shown in Figure 1.

Table 1: Formulations employed during the polymerization reactions (M1: Bulk and S1, S2: Suspension).

	M1	S1	S2
Styrene (g)	91.0	230.0	460.0
Water (g)	-	525.0	1058.0
BPO (g)	3.40	8.60	17.2
DBSS (g)	-	0.24	0.22
PVP (g)	-	0.80	0.80
Temperature (°C)	90	90	90
Stirring (rpm)	-	600	450

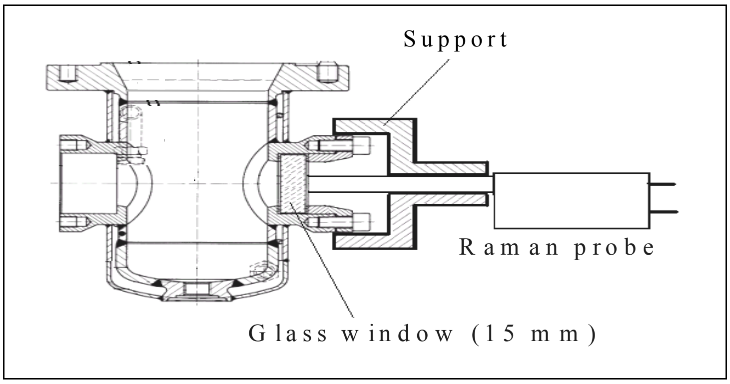


Figure 1: Illustration of the Raman probe connected to the reactor window.

Bulk Polymerization Reactions

The bulk polymerization reactions were carried out inside ampoules according to the formulation shown in Table 1. They were carried out following the methodology described by Dubé et al. (1990). The styrene bulk polymerization reactions were conducted in glass ampoules of 96 mm length, internal diameter of 10 mm and 0.95 mm thick glass walls. After preparing the reaction medium, the ampoules were loaded with 3 ml each, sealed and immersed into a thermostatic bath at the temperature indicated for the reaction (Table 1). To stop the reaction, each ampoule was taken from the bath and immediately immersed into an ice/ethanol bath to interrupt the polymerization by cooling.

In order to determine the conversion, the following gravimetric procedure was used: the samples were taken from the ampoules and placed in previously weighed Petri culture dishes. These dishes were weighed again, this time with the samples. A small amount of inhibitor (p-benzoquinone) (approximately 0.01g) was added to each dish, to avoid that the polymerization reaction continued. The samples were diluted with toluene and, afterwards, introduced into a vacuum oven with controlled temperature (100ºC) and vacuum (400 mmHg) to evaporate the solvent and the residual monomer. At the end, the dishes were weighed again and, by weight difference, it was possible to determine the polymer content and consequently the conversion of the sample analyzed.

RESULTS AND DISCUSSION

Comparison of the Gravimetric Data Obtained for Bulk and Suspension Polymerizations

Figure 2 shows a comparison between the conversion data obtained by the gravimetric procedure during the suspension polymerization, and the conversion data obtained for the bulk polymerizations in ampoules.

Observing the data in Figure 2, it is possible to note a difference in the reaction rate that increases with the progress of the reaction. Both reactions were conducted with the same initiator/monomer ratio; therefore, the difference in the reaction rate is possibly related to the reaction temperature. The styrene polymerization reaction is highly exothermic and, as the reaction proceeds, the viscosity of the reaction media increases rapidly, reducing the heat transfer coefficient. Additionally, the rise in viscosity also causes an increase of the reaction rate due to the gel effect.

Suspension polymerizations present lower viscosities than bulk polymerizations because of the use of water as the continuous medium (polymer particles are dispersed in the aqueous phase). This lower viscosity of the continuous medium enhances the heat exchange capacity and, consequently, improves the temperature control of the reactor. Besides that, in suspension polymerizations the ratio between the surface area of the polymer particles and the particle volume is much higher than the ratio between the thermal exchange area of the ampoules and the volume of the reaction medium of the bulk polymerizations. Therefore, the effective thermal exchange area of the suspension polymerization (polymer phase) is much higher than that of the bulk polymerization. Additionally, in bulk polymerizations, the thermostatic bath is kept at the desired reaction temperature, but the temperature of the reaction medium inside the ampoules does not remain constant due to the viscosity increase with the progress of the reaction, which causes a reduction in the thermal exchange efficiency. These factors favor the appearance of a temperature gradient inside the ampoules and an increase in the average reaction temperature. The reaction temperature increase, in turn, favors an increase on the reaction rate, which helps to explain why the bulk polymerization rate is higher than the rate observed in styrene suspension polymerizations.

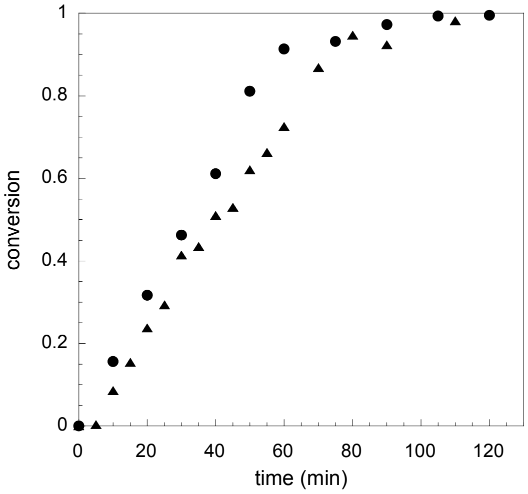


Figure 2: Comparison of gravimetric data obtained during styrene suspension and bulk polymerizations. ▲ S1 Suspension polymerization; ● M1 Bulk polymerization.

The temperature of the reaction medium was recorded continuously during both polymerizations by a thermocouple coupled to a data acquisition board. The thermocouple was placed inside an ampoule during the bulk reaction and immersed in the middle of the reaction medium during the suspension polymerization. Figure 3 shows the evolution of the temperature during both reactions. It can be observed that the temperature of the suspension polymerization decreased at the beginning of the reaction with the addition of the initiator dissolved in styrene and, a few minutes later, of DBSS and PVP, which were all fed at room temperature to the reactor. In the bulk polymerization system the initiator was already in the ampoules and the temperature rapidly increased, staying 2 to 3°C above that of the suspension polymerization reaction up to 60 minutes of reaction when 90% conversion was reached in the bulk polymerization**.**

In order to verify if this difference between the reaction temperatures was sufficient to explain the difference observed in the conversion, simulations were carried out with a mathematical model of styrene homopolymerizations using the experimental temperature profiles obtained for both reactions (*see* Appendix). Figure 4 compares simulation and experimental conversion results of both bulk and suspension polymerizations and a good agreement can be observed for both reactions. This indicates that the difference of reaction temperature observed between these two systems is able to explain the differences in the reaction rate.

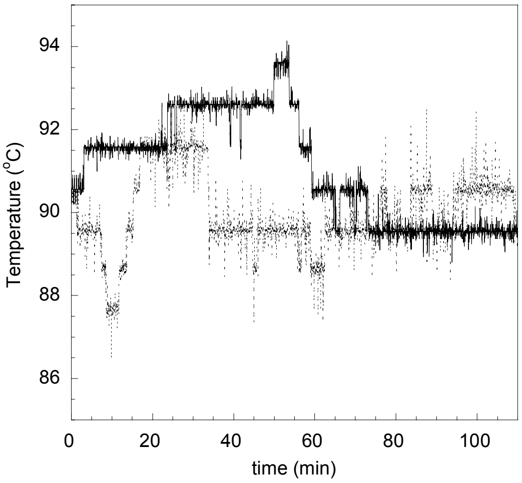


Figure 3: Evolution of the temperature of the reaction medium during M1 Bulk polymerization (—) and during S1 Suspension polymerization (- - -).

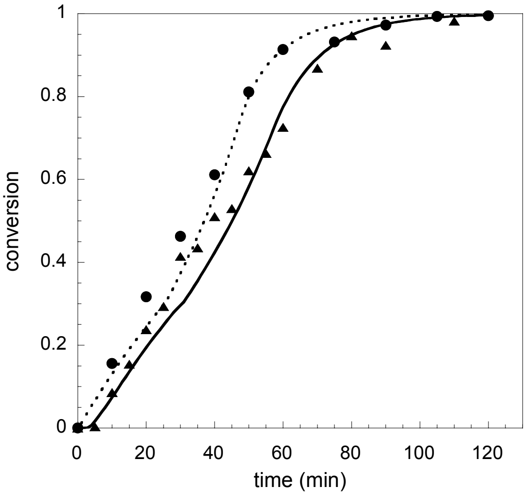
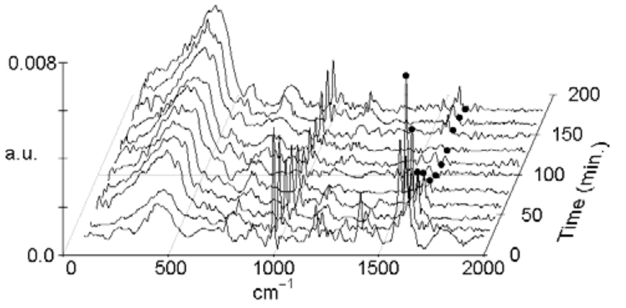


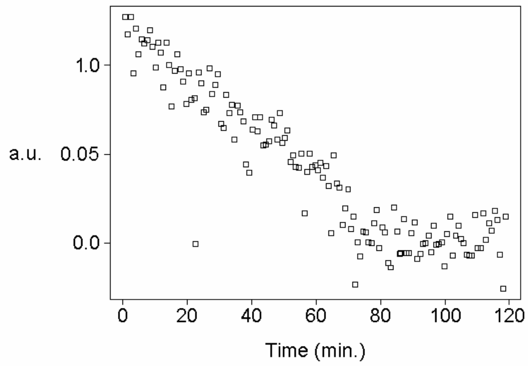
Figure 4: Comparison between experimental conversion (gravimetry) (dots) and theoretical conversion (mathematical model) (lines). ▲ and (—) S1 Suspension polymerization; ● and (- - -) M1 Bulk polymerization.

Results Obtained by Raman Spectroscopy

Raman spectroscopy is a light scattering based technique and represents an attractive method to monitor polymerizations of vinyl monomers, since the Raman band corresponding to the C=C double bond, which disappears during the polymerization reaction, exhibits a strong signal, as shown in Figure 5. Therefore, in homopolymerization reactions, the conversion can be estimated directly by Raman spectroscopy as the relation between the intensity of the spectra and monomer concentration is linear (Santos et al., 2004; Reis et al., 2005).



(a)



(b)

Figure 5: (a) Spectra collected during the suspension polymerization reaction, dots correspond to the band due to the stretching of the double bond; (b) Area corresponding to the C=C double bond stretch. (Reproduced with permission from Ind. Eng. Chem. Res. 2004, 43, 7282-7289. Copyright 2004 American Chemical Society)

Comparison Between Conversion Estimated by Raman Spectroscopy and Off-Line Gravimetric Conversion

The precise off-line quantification of monomer conversion by gravimetry and the conversion monitoring during suspension polymerization reactions are quite difficult due to the high heterogeneity of the reaction medium and the tendency of the particles to agglomerate rapidly when stirring is stopped. The major problem of gravimetry is to collect representative samples from the reactor. In contrast, Raman monitoring through the reactor window is non-invasive and, since no sampling is required, presents the advantage of the stirring, which avoids the decantation of polymer particles and reduces the heterogeneity of the medium. Raman spectra, collected during the reactions, were obtained by a small number of scans in order to reduce the spectral acquisition time, which results in a low signal/noise ratio. Therefore, a dynamic filter was used. This filter was only applied after the collection of the first five Raman spectra (4 minutes and 15 seconds of reaction), and the five concentration values estimated up to this point were used in the first filter application. This procedure was applied successively after the acquisition of each new spectrum, the predicted value being corrected by the spline filter, using all the raw points evaluated up to that point. It is important to emphasize that this filtering procedure was proposed for on-line use; therefore, the corrections are not applied backwards. The use of this filter is indicated to reduce the variability of the estimation (Santos et al., 2004).

Figure 6 shows the comparison between off-line gravimetric conversion measurements and Raman monitoring of conversion during a styrene suspension polymerization (S2). In this figure an excellent agreement can be observed between Raman estimations and gravimetric data. Gravimetric data were obtained up to 75 minutes of reaction. After this point, the valve located at the bottom of the reactor used to collect samples was obstructed with polystyrene and could not be used any longer. It is important to emphasize that the conversion estimations by Raman spectroscopy did not require any reference method. In this way, one measurement method corroborates the results of the other one.

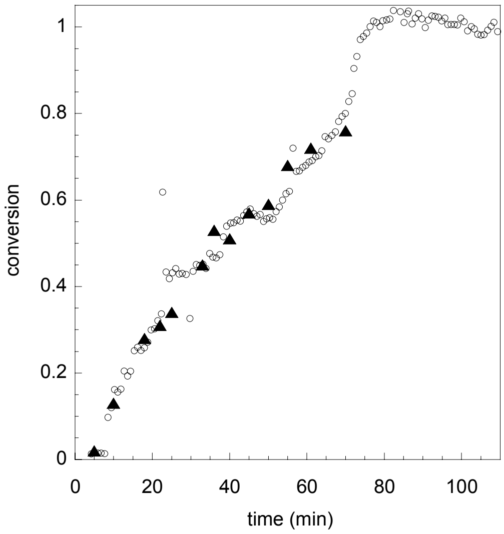


Figure 6: Comparison of the evolution of monomer conversion during S2 Suspension polymerization reaction. (○) On-line estimation by Raman spectroscopy with a dynamic smoothing spline filter; (▲) Off-line gravimetry. (Reproduced with permission from Ind. Eng. Chem. Res. 2004, 43, 7282-7289. Copyright 2004 American Chemical Society)

CONCLUSION

The methodology employed in this work to determine the conversion evolution of a suspension polymerization reaction by gravimetry was quite effective, as confirmed by the good agreement with on-line conversion monitoring using Raman Spectroscopy.

The comparison between suspension and bulk styrene homopolymerizations conducted with the same initiator/monomer ratio showed that bulk polymerization in ampoules, which is frequently used to obtain the conversion evolution of suspension polymerizations, can present a higher polymerization rate than the real rate of a suspension polymerization. This occurs due to the non-homogeneous thermal effects of the bulk reaction even for systems where the gel effect is not very pronounced. The effect of the differences in the reaction temperature on the evolution of conversion was also confirmed by simulation results. Therefore, caution is recommended when bulk polymerization in ampoules is used for the kinetic study of styrene suspension polymerization, since in this latter case the reaction temperature control is much more effective and, consequently, the reaction rate does not follow the same course as in the bulk polymerization in ampoules.

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APPENDIX

Polymerization Model

The same model is used for the simulations of suspension and bulk styrene polymerization reactions, as styrene presents a very low solubility in the aqueous phase and, consequently, no reaction in the aqueous phase is considered. The kinetic mechanism takes the following reactions into account: initiation, propagation and termination. The assumptions listed below are used in the model:

1. kinetic constants do not depend on chain length;
2. the pseudo-steady-state hypothesis is valid for radicals;
3. the reactor operates non-isothermally;
4. the tank reactor is perfectly mixed.

The mass balance equations used to describe the batch bulk and suspension styrene polymerizations were written as:

$$\frac{1}{V}\frac{d\left(V[I]\right)}{dt}=-k_d[I] \tag{1}$$

$$\frac{1}{V}\frac{d\left(V[R]\right)}{dt}=2fk_d[I]-k_t[R]^2=0 \tag{2}$$

$$\frac{1}{V}\frac{d\left(V[M]\right)}{dt}=-k_p[R][M] \tag{3}$$

$$\frac{1}{V}\frac{d\left(V[P]\right)}{dt}=k_p[R][M] \tag{4}$$

where T is the reaction temperature, V is the volume of the organic phase, [ ] refers to concentration, I is the initiator, R is the free radical, M is the monomer, P is the polymer and f is the efficiency of free radical formation from the decomposition of the initiator and is assumed equal to 0.5.

The following equations are used to take the volume contraction into account:

$$\frac{dV}{dt}=-\frac{V}{\bar{\rho}}\frac{d\bar{\rho}}{dt} \tag{5}$$

$$\bar{\rho}=\rho_M[M]+\rho_P[P] \tag{6}$$

$$\frac{d\bar{\rho}}{dt}=\rho_M\frac{d[M]}{dt}+\rho_P\frac{d[P]}{dt} \tag{7}$$

where ρ_M and ρ_P, are, respectively, the densities of the monomer and of the polymer density. Both densities were considered constant (ρ_M = 0.835 g/cm^3 and ρ_P = 1.0387 g/cm^3) as the reaction temperature range is narrow.

The following coefficients are used to describe the polymerization kinetics in the polymer phase (Brandrup & Immergut, 1989):

$$k_p=1.89\times10^{12}\exp\left[-10400/\left(1.987T\right)\right],\quad [\text{mol/(L.s)}] \tag{8}$$

$$k_{t0}=6.52\times10^{16}\exp\left[-8870/\left(1.987T\right)\right],\quad [\text{mol/(L.s)}] \tag{9}$$

$$k_d=1.4\times10^{14}\exp\left[-125700/\left(8.314T\right)\right],\quad [\text{1/s}] \tag{10}$$

The gel effect (x_{gel}), which accounts for the decrease of the termination rate, is computed as proposed by Hui and Hamielec (1972):

$$\begin{aligned} x_{gel}&=\exp\left[-2\left(b_s\phi_p+c_s\phi_p^2+d_s\phi_p^3\right)\right]\\ b_s&=2.57-0.0055T\\ c_s&=9.56-0.0176T\\ d_s&=-3.03+0.00785T \end{aligned} \tag{11}$$

where ϕ_p is the volume fraction of polymer in the polymer phase.

$$k_t=x_{gel}k_{t0} \tag{12}$$

The developed model was implemented in FORTRAN and the system of differential equations was solved using the DASSL solver (Petzold, 1982).