DOI: 10.1002/masy.200651119

Initiation Efficiency Reduction in Semicontinuous Styrene and Butyl Acrylate Emulsion Copolymerization Reactions

Wilson H. Hirota,[1] *Reinaldo Giudici,*[1] *Cláudia Sayer**[2]

Summary: The decrease of initiation efficiency (radical entry efficiency) during seeded emulsion copolymerizations of styrene and butyl acrylate with different residual monomer reduction strategies was evaluated. Experiments were carried out using 50 and 99wt.% of styrene in monomer feed stream. Simulations were performed with a detailed mathematical model of the process that takes into account the diffusion control of initiation, propagation and termination. Results showed that the radical entry into polymer particles is strongly influenced by the aqueous phase kinetics and by the monomer solubility in aqueous phase. Simulation results were compared to experimental results of residual monomer and showed that the residual monomer content can be reduced by a temperature increase at the end of the polymerization. However, an additional feeding of more initiator, even when combined with such an increase of temperature, did not lead to a smaller residual monomer content due, mainly, the kinetic of termination in aqueous phase and radical anchoring. A model that accounts for the reduction of initiator efficiency (free radical entry efficiency) was successfully used to explain the behavior of the experimental observations and was able to correctly predict the qualitative trends of the effectiveness of different residual monomer reduction strategies.

Keywords: diffusion control; emulsion polymerization; entry efficiency; initiation efficiency; latices; residual monomer

Introduction

Emulsion polymerization is a heterogeneous free-radical polymerization technique that has as main advantages the high polymerization rate, the production of high molecular weight polymers and the utilization of water as continuous phase, permitting better dissipation of the heat of reaction and minimization of the toxic effects. Due to these particularities, emulsion polymerization is one of the most used techniques, mainly in the paint, adhesive and paper coatings industries. However, as in any free radical polymerization process, the conversion of monomer into polymer does not occur in a complete manner, resulting in an accumulation of residual monomer in the final polymer product, which can lead to process and environmental problems and to the necessity of removing the unreacted monomer. Despite the importance of this subject in industrial scope, few works have been published regarding this issue and the mechanisms involved in high conversion polymerization.

Araújo et al.[1] analyzed the main causes that may lead to the accumulation of

---

[1] Universidade de São Paulo, Escola Politécnica, Department of Chemical Engineering, Av. Prof. Luciano Gualberto, trav. 3, no. 380, 05508-900 São Paulo, Brazil; Fax: (+55) 11 3813-2380;
E-mail: wilson.hirota@poli.usp.br; rgiudici@usp.br

[2] Universidade Federal de Santa Catarina, Department of Chemical Engineering and Food Engineering, Florianópolis, Santa Catarina, Brazil
Fax: (+55) 48 3331-9687
E-mail: csayer@enq.ufsc.br

monomer and the most used techniques employed in the reduction of the residual monomer content in the final product. Among the causes of the residual monomer accumulation, the authors quote the cage effect and the glass effect, related directly with strong variations in the viscoelastic properties of the reaction medium, which in turn depend of conversion, turning the process into to a diffusion-controlled one.

The glass effect, which is a diffusional phenomenon, occurs at high conversions due to the increase of viscosity when the reaction is carried out below the polymer glass transition temperature. This phenomenon is responsible for drastic reduction in the mobility of monomer and polymer molecules in the reaction medium and, consequently, to a decrease of the propagation rate constant, which prevents the reaction from reaching 100% conversion.

In emulsion polymerization water-soluble initiators are most commonly used and, therefore, the generation of primary free radicals occurs in the aqueous phase, far from the major locus of polymerization located in the interior of the polymer particles. As a consequence, kinetics of species present in the aqueous phase control many events such as the entry of free radicals into the particles, the fate of free radicals desorbed from particles and of free radicals species originated from initiator, particle nucleation and re-nucleation.[2] Although the kinetics of processes taking place in the aqueous phase, specially the entry of radicals into polymer particles, show great importance on the final latex properties, this process is still poorly understood due, mainly, to a lack of accurate experimental entry rate coefficient data.[3] Therefore, several theories were proposed to explain and to quantify the radical entry mechanism into polymer particles such as diffusion-control model, displacement of surfactant theory, hypothesis of entry of radicals through a colloidal interaction between a latex particle and an oligomeric aqueous-phase radical and the control by aqueous phase growth model.[4]

The goal of the present work is to analyze the influence of the aqueous phase kinetics on the decrease of radical entry efficiency during seeded styrene/butyl acrylate copolymerizations performed with 50% and 99% styrene in monomer feed stream and on the residual monomer content after the implementation of the residual monomer reduction strategies.

Theoretical Approach

In the present work, a generalized mathematical model proposed by Keramopoulos and Kiparissides[5] for bulk free-radical copolymerization reactions was combined with a detailed mathematical model of emulsion copolymerization reactions developed by Araújo and Giudici[6] and previously validated for emulsion copolymerizations reactions by Hirota et al.[7] This model was used to simulate semicontinuous emulsion copolymerizations of styrene and butyl acrylate in order to observe the influence of diffusional control and reduction of the initiation efficiency on monomer conversion and on residual monomer content.

The initiation efficiency of primary free radicals follows the original developments of Maxwell et al.[3] for the entry rate coefficient considering that this parameter is influenced by the particle surface characteristics and by the kinetics of the aqueous phase. Thus, the entry process for copolymerization reactions is described by:
initiator decomposition:

$$S_2O_8^{2-} \xrightarrow{k_d} 2SO_4^- \tag{1}$$

initial propagation step:

$$SO_4^- + M_1 \xrightarrow{k_{p1}^{aq}} M_1^\bullet \tag{2a}$$

$$SO_4^- + M_2 \xrightarrow{k_{p2}^{aq}} M_2^\bullet \tag{2b}$$

subsequent propagation:

$$M_{i,1}^\bullet + M_1 \xrightarrow{k_{p11}^{aq}} M_{i+1,1}^\bullet \tag{3a}$$

$$M_{i,1}^\bullet + M_2 \xrightarrow{k_{p12}^{aq}} M_{i+1,2}^\bullet \tag{3b}$$

$$M_{i,2}^\bullet + M_1 \xrightarrow{k_{p21}^{aq}} M_{i+1,1}^\bullet \tag{3c}$$

$$M_{i,2}^\bullet + M_2 \xrightarrow{k_{p22}^{aq}} M_{i+1,2}^\bullet \tag{3d}$$

Termination entry:

$$M^{\bullet}_{i,1} + T^{\bullet} \xrightarrow{k^{aq}_{t1}} \text{inert products},\ i < z \qquad (4a)$$

$$M^{\bullet}_{i,2} + T^{\bullet} \xrightarrow{k^{aq}_{t2}} \text{inert products},\ i < z \qquad (4b)$$

$$M^{\bullet}_{z} + \text{latex particle} \xrightarrow{\rho} \text{entry} \qquad (5)$$

where M is a monomer unit, $M^{\bullet}_{i}$ a radical of monomer i with a sulfate group, $M^{\bullet}_{i,j}$ an oligomeric radical containing i monomer units and monomer j as terminal group, z the number of monomer units a primary free radical must add before it may enter a latex particle, which depends of reaction temperature and monomer solubility in the aqueous phase[8], and $M^{\bullet}_{z}$ the entering group, $T^{\bullet}$ is any aqueous phase free radical, k_d the first-order initiator decomposition rate coefficient, k^{aq}_{pi} the propagation rate coefficient of a radical of monomer i with a sulfate group, and k^{aq}_{pij} and k^{aq}_{ti} are, respectively, the aqueous phase rate coefficients of propagation between a radical with terminal group of monomer i and a monomer j; and aqueous phase termination rate coefficients of the polymeric radical with terminal group of monomer i. The higher the value of z, the longer the oligomer may remain in the aqueous phase and, consequently, the higher is the probability of aqueous phase termination to occur.

Due to the possibility of termination in the aqueous phase (eq. 4), not all radicals formed by thermal decomposition of the initiator will enter into the particles. This is more critical at high conversions when monomer concentration in the aqueous phase is low and, consequently, radicals remain a longer time in the aqueous phase before reaching a size long enough to enter into a particle. Thus, the initiation efficiency (entry efficiency) will be strongly influenced by the aqueous phase kinetics and by values of z. The entry efficiency (f) can be calculated by the relation:

$$f = \frac{[R^{ent}_{T}]_{aq}}{[R^{*}_{T}]_{aq}} \qquad (6)$$

where $[R^{ent}_{T}]_{aq}$ is the total concentration of radicals in the aqueous phase that can enter micelles or polymer particles and $[R^{*}_{T}]_{aq}$ is the total concentration of radical in the aqueous phase if all radicals generated by thermal decomposition of initiator would enter micelles or polymer particles.

The kinetic mechanism used to represent the emulsion polymerization process considers the following reactions: initiation, propagation, transfers to monomer and to polymer and termination. The following assumptions are used to derive the model equations:

- kinetic constants in the aqueous and polymer phases are the same;
- kinetic constants do not depend on chain length;
- the pseudo-steady-state hypothesis is valid for radicals;
- particles are generated by both homogeneous and micellar nucleation mechanisms;
- radicals that enter micelles or polymer particles are of length z and $j_{crit} - 1$;
- radicals generated by initiation or chain transfer to monomer present similar reactivities;
- radical reactivity is given by the last monomeric unity;
- monomer concentration in the polymer particles, monomer droplets and aqueous phase are at thermodynamic equilibrium

For the sake of brevity, only the model equations related to the calculation of entry efficiency will be presented. Full details of the model are given elsewhere.[6]

The total concentration of radicals in the aqueous phase that can be enter a particle ($[R^{ent}_{T}]_{aq}$) is computed by the iterative procedure developed by Araújo and Giudici[6] based on two different critical radical lengths proposed by Gilbert[8] as follows.

The concentration of the radicals with one monomeric unit ($[R_1]_{aq}$) is:

$$[R_1]_{aq} = \left(\frac{\dfrac{2 \cdot [I]_{aq} \cdot f_I \cdot k_d}{v_{aq}} + \dfrac{k_f \cdot [M]_p \cdot \overline{n} \cdot N_p}{v_{aq} \cdot Na}}{k_p \cdot [M]_{aq} + k_t \cdot [R_T]_{aq}} \right) \qquad (7)$$

The concentration of radicals of length $j_{crit}-1$ is given by:

$$[R_{j_{crit}-1}] = [R_1]_{aq} \cdot \left(\frac{k_p \cdot [M]_{aq}}{k_p \cdot [M]_{aq} + k_t \cdot [R_T]_{aq}}\right)^{(z-2)} \cdot \left(\frac{k_p \cdot [M]_{aq}}{\Psi}\right)^{(j_{crit}-z)} \tag{8}$$

$$\Psi = k_p \cdot [M]_{aq} + k_{abs} \cdot \frac{N_p}{v_{aq} \cdot Na} + k_{abs}^m \cdot \frac{N_{mic}}{v_{aq} \cdot Na} + k_t \cdot [R_T]_{aq} \tag{9}$$

The total concentration of radicals in aqueous phase that can enter a micelle or a particle (radicals with length between z and $j_{crit}-1$) is:

$$[R_T^{ent}]_{aq} = [R_1]_{aq} \cdot \left(\frac{k_p \cdot [M]_{aq}}{k_p \cdot [M]_{aq} + k_t \cdot [R_T]_{aq}}\right)^{(z-2)} \sum_{j=z}^{j_{crit}-1} \left(\frac{k_p \cdot [M]_{aq}}{\Psi}\right)^{(j-z+1)} \tag{10}$$

The total concentration of radicals in the aqueous phase (all lengths) can be expressed as:

$$[R_T]_{aq} = [R_1]_{aq} \left[1 + \sum_{j=2}^{z-1} \left(\frac{k_p \cdot [M]_{aq}}{k_p \cdot [M]_{aq} + k_t \cdot [R_T]_{aq}}\right)^{(j-1)}\right] + [R_T^{ent}]_{aq} \tag{11}$$

The entry rates of radicals into particles (k_{abs}) and micelles (k_{abs}^m) in eq. (9) are given by:

$$k_{abs} = 4 \cdot \pi \cdot D_w \cdot r_p \cdot Na \cdot f_{abs} \tag{12}$$

$$k_{abs}^m = 4 \cdot \pi \cdot D_w \cdot r_m \cdot Na \cdot f_{abs}^m \tag{13}$$

where D_w, r_p, f_{abs}, r_m and f_{abs}^m represent, respectively, the diffusion coefficient in the aqueous phase, the radius of swollen polymer particle,[6] the absorption efficiency of aqueous phase radicals by particles, the radius of one micelle and the absorption efficiency of aqueous phase radicals by the micelles.

In the present work, using seeded reactions, the particle formation by micellar nucleation was negligible. The evolution of particle number (N_p), and of initiator concentration in aqueous phase ($[I]_{aq}$) are computed by population balance and mass balance equations, respectively. The average number of radicals per polymer particle ($\overline{n}$) is computed by iterative method proposed by Ugelstad et al.[9] Parameters f_I and k_d in eq. (7) are the cage-effect initiator efficiency (adopted equal to 1) and the rate constant for initiator decomposition, respectively.

The aqueous phase volume (v_{aq}) and monomer concentration in the polymer particle ($[M]_p$) and monomer concentration in the aqueous phase ($[M]_{aq}$) are calculated by iterative method proposed by Omi et al.[10] using the partition coefficients of the monomer in monomer drops and polymer phase.

In eqs. (7)–(11) the following pseudo-kinetic rate constants are used to describe the copolymerization kinetics in the polymer particles (and, analogously, for the aqueous phase):

Propagation:

$$k_p = \sum_{i=A,B} (k_{pAi} \cdot P_{Aj} + k_{pBi} \cdot P_{Bj}) \tag{14}$$

Chain transfer to monomer:

$$k_f = \sum_{i=A,B} (k_{fAi} \cdot P_{Aj} + k_{fBi} \cdot P_{Bj}) \tag{15}$$

Termination:

$$k_t = k_{tAA} \cdot P_{Aj}^2 + 2 \cdot k_{tAB} \cdot P_{Aj} \cdot P_{Bj} + k_{tBB} \cdot P_{Bj}^2 \tag{16}$$

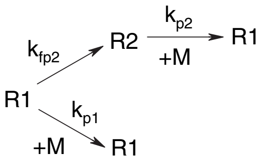
where subscript j stands for the phase (aqueous or polymer particles) and P_{Aj} and P_{Bj} are the relative frequencies of radicals containing monomeric units of type A or B at the active and can be expressed as follows:

$$P_{Aj} = \frac{k_{pBA}[A]_j}{k_{pBA}[A]_j + k_{pAB}[B]_j} \tag{17}$$

$$P_{Bj} = 1 - P_{Aj} \tag{18}$$

The propagation and termination rate constants for polymer phase were expressed in terms of reaction and diffusion limitations and were calculated based on the work of Keramopoulos and Kiparissides.[5] The diffusion of the reactive species into polymer particle is calculated in terms of the continuous change of the transport properties of the reaction medium during the copolymerization reactions using the free-volume model originally proposed by Ventras and Duda.[11]

Besides, intramolecular chain transfer for butyl acrylate also was considered in the calculation of the propagation kinetics. Plessis et al.[12] showed that the reactivity of tertiary carbon radicals originated by intramolecular chain transfer (R_2) is much lower than that secondary radicals (R_1) and it is reasonable to expect that the activity of the alkylated acrylate radical, R_2, will be much lower than of an acrylate radical, R_1. The following reaction scheme was proposed by Plessis et al.[12]



where k_{fp2} is the intramolecular chain transfer reaction and k_{p1} and k_{p2} are the propagation rate constants of radicals R_1 and R_2, respectively.

Thus, the Plessis et al.[12] showed that the pulsed laser polymerization (PLP) techniques do not provide satisfactory values of k_p at temperatures above 30 °C and proposed that the effective intrinsic propagation rate constant for butyl acrylate be computed by:

$$k_{p0BB} = k_{p1} \cdot P_1 + k_{p2} \cdot P_2 \tag{19}$$

where P_1 and P_2 are the probabilities of having a radical of type R_1 and R_2, respectively, given by:

$$P_1 = \frac{k_{p2} \cdot [M]_j}{k_{fp2} + k_{p2} \cdot [M]_j} \tag{20}$$

$$P_2 = 1 - P_1 \tag{21}$$

where $[M]_j$ is the concentration of monomer in the phase j (aqueous phase, and polymer particles) and is implicitly assumed that the rates of termination and transfer to monomer by radicals of type R_2 are negligible.

In eq. 6 the value of $[R_T^*]_{aq}$ is computed considering that the total concentration of radicals in aqueous phase that can enter a micelle or a particle is equal to concentration of radicals formed by thermal decomposition of initiator:

$$[R_T^{ent}]_{aq} = \frac{2 f_I k_d [I]_{aq}}{k_{abs} \frac{N_p}{v_{aq} Na}} \tag{22}$$

Parameters used in the simulations are presented in Table 1.

Experimental Section

In order to verify the influence of aqueous phase kinetics on the initiator efficiency and on the effect of residual monomer content reduction strategies different seeded emulsion copolymerization reactions with styrene (St)/butyl acrylate (BA) ratios equal to 50/50 and 99/01 were simulated with the mathematical model described above. The results obtained were compared with experimental results obtained under the same conditions used in the simulations.

Polymer seeds were produced in batch styrene homopolymerization reactions, following the formulation shown in Table 2 and conducted at 80 °C during the first 60 minutes and then at 90 °C during the final 180 minutes of reaction to ensure the complete initiator decomposition and to increase the monomer conversion. The use of seeds enhances the reproducibility of particle size and number and thus allows a better control of polymerization rate.[25]

The seeded semicontinuous styrene and butyl acrylate emulsion copolymerization reactions were carried out at 70 °C, with

Table 1.
Parameters used in the simulations (A, styrene/B butyl acrylate).

Parameter		Value	Unit	Reference
k_d	rate constant for initiator decomposition	$2,56 \times 10^{15} \cdot e^{\left(\frac{-3,32}{RT}\right)}$	$1/s$	Penlidis[13]
k_{pAA}	rate constant for propagation of radical type *A* with a radical type *A*	$5,70 \times 10^{11} \cdot e^{\left(\frac{-9805}{RT}\right)}$	$cm^3/gmol \cdot s$	Gao and Penlidis[14]
k_{pBB}	rate constant for propagation of radical type *B* with a radical type *B*	$2,05 \times 10^{7} \cdot e^{\left(\frac{-4270}{RT}\right)}$	$cm^3/gmol \cdot s$	Plessis et al.[15]
k_{pAB}	rate constant for propagation of radical type *A* with a radical type *B*	k_{pAA}/r_A	$cm^3/gmol \cdot s$	Araújo and Giudici[6]
k_{pBA}	rate constant for propagation of radical type *B* with a radical type *A*	k_{pBB}/r_B	$cm^3/gmol \cdot s$	Araújo and Giudici[6]
k_{p2}	rate constant for propagation of tertiary carbon radicals of type B	100×10^3	$cm^3/gmol \cdot s$	Plessis et al.[12]
k_{tAA}	rate constant for termination of radical type *A* with radical type *A*	$6,52 \times 10^{16} \cdot e^{\left(\frac{-8870}{RT}\right)}$	$cm^3/gmol \cdot s$	Paquet and Ray[16]
k_{tBB}	rate constant for termination of radical type *B* with radical type *B*	$1,679 \times 10^{7} \cdot e^{\left(\frac{-2800}{RT}\right)}$	$cm^3/gmol \cdot s$	McKenna et al.[17]
k_{tAB}	rate constant for termination of radical type *A* with radical type *B*	$\sqrt{k_{tAA} \cdot k_{tBB}}$	$cm^3/gmol \cdot s$	Ginsburger et al.[18]
k_{tBA}	rate constant for termination of radical type *B* with radical type *A*	$\sqrt{k_{tAA} \cdot k_{tBB}}$	$cm^3/gmol \cdot s$	Ginsburger et al.[18]
k_{fAA}	rate constant for chain transfer of radical type *A* to monomer *A*	$1,0 \times 10^{-5} \cdot k_{pAA}$	$cm^3/gmol \cdot s$	Paquet and Ray[16]
k_{fBB}	rate constant for chain transfer of radical type *B* to monomer *B*	$5,0 \times 10^{-6} \cdot k_{pBB}$	$cm^3/gmol \cdot s$	Paquet and Ray[16]
k_{fAB}	rate constant for chain transfer of radical type *A* to monomer *B*	$\sqrt{k_{fAA} \cdot k_{fBB}}$	$cm^3/gmol \cdot s$	Ginsburger et al.[18]
k_{fBA}	rate constant for chain transfer of radical type *B* to monomer *A*	$\sqrt{k_{fAA} \cdot k_{fBB}}$	$cm^3/gmol \cdot s$	Ginsburger et al.[18]
k_{fp2}	rate constant for intramolecular chain transfer	$3.5 \times 10^{7} e^{\left(-\frac{6998}{RT}\right)}$	$cm^3/gmol \cdot s$	Plessis et al.[15]
k_{fpAA}	rate constant for chain transfer of radical type A to copolymer	$2,2 \times 10^{-4} \cdot k_{pAA}$	$cm^3/gmol \cdot s$	Brandrup and Immergut[19]
k_{fpBB}	rate constant for chain transfer of radical type A to copolymer	$1,51 \times 10^{-3} \cdot k_{pBB}$	$cm^3/gmol \cdot s$	Brandrup and Immergut[19]
r_A	Reactivity ratio of monomer A	0,75		Gugliotta et al.[20]
r_B	Reactivity ratio of monomer B	0,20		Gugliotta et al.[20]
$\rho_A(*)$	Density of monomer A	$0.924 - 9.18x10^{-6}T$	g/cm^3	Tefera et al.[21]
$\rho_B(*)$	Density of monomer B	$0,9197 - 0,00104T$	g/cm^3	Barudio et al.[22]
D_{wA}	Diffusion coefficient of monomer A in the aqueous phase	$1,0 \times 10^{-5}$	cm^2/s	Echevarria et al.[23]

Continues

Table 1.
Continued

Parameter		Value	Unit	Reference
D_{wB}	Diffusion coefficient of monomer B in the aqueous phase	$1,1 \times 10^{-5}$	cm^2/s	Araújo and Giudici[6]
$j_{crit}A$	critical length of radical	3,0		Gilbert[8]
$j_{crit}B$	critical length of radical	8,0		Gilbert[8]
k^p_{mA}	Partition coefficient of the monomer A in polymer particles/aqueous phase	1500		Echevarria et al.[23]
k^p_{mB}	Partition coefficient of the monomer B in polymer particles/aqueous phase	460		Gugliotta et al.[20]
k^d_{mA}	Partition coefficient of the monomer A in monomer droplets/aqueous phase	2700		Echevarria et al.[23]
k^d_{mB}	Partition coefficient of the monomer B in monomer droplets/aqueous phase	705		Gugliotta et al.[20]
PM_A	Molecular weight of monomer *A*	104,54	$g/gmol$	Brandrup and Immergut[19]
PM_B	Molecular weight of monomer *B*	128,17	$g/gmol$	Brandrup and Immergut[19]
z	Minimum length of radical for radical entry into micelles and polymer particles	3,0		Van Berkel et al[24]

(∗)Temperature in °C.

Table 2.
Formulation used in batch reactions to produce polymer seeds.

Reactants	Initial charge (g)	Initiator solution (g)[a)]
Water	1812.49	134.82
Sodium lauryl sulfate (SLS)	70.11	
Na_2CO_3	1.89	
St	679.48	
$Na_2S_2O_8$		1.21

[a)] Added at reaction start.

agitation frequency of 250 rpm and flow rates of monomers and initiator adjusted to complete the feeding in 3 hours. During this monomer feeding period, all reactions followed the same formulation presented in Table 3. The residual monomer reduction strategies were applied after 180 minutes (t_{feed}), when the temperature was increased from 70 °C to 80 °C, and/or 220 minutes, when more initiator was fed to the reactor. The strategies are summarized in Figure 1.

In order to become more similar to the industrial process and, consequently, to allow a more realistic comparison of the residual monomer reduction strategies, these reactions were carried out with a high solids content.

Styrene and butyl acrylate concentrations were measured by head-space gas chromatography (HS-GC - Shimadzu), average particle sizes were obtained by dynamic light scattering (Coulter N4 Plus), gel contents were measured by solid-liquid extraction (Sohxlet) using chloroform as solvent, and grains contents were obtained by filtration using a 45 μm sieve.

Results and Discussion

Figure 2 show the evolutions of free radical entry efficiency (Figure 2a) and the concentration of initiator in aqueous phase (Figure 2b) obtained by simulations for both base reactions with St/BA ratios equal to 50/50 and 99/01.

Figure 2a shows that at the beginning of the reaction, entry efficiency is almost 100%, indicating that aqueous phase ter-

Table 3.
Formulation used in seeded semicontinuous copolymerization reactions.

Reactants	Initial charge (g)	Feed 1 (g)		Feed 2 (g)
		50 %wt St	99 %wt St	
Water	1863.5			287.34
Anionic emulsifier	2.0			16.83
Non ionic emulsifier	0.5			4.21
Initiator	0.7			10.06
Buffer	0.448			6.44
Seed	90			
St		608.26	1228.5	
BA		608.26	12.4	
Acrylic Acid		24.33	24.8	

mination is not significant due to the low concentration of radicals. For the reaction with St/BA=50/50, entry efficiency remains almost constant due to the semicontinuous addition of initiator (Figure 2b), which favors the continuos generation of oligomeric radicals. When initiator feeding was stopped, at higher monomer conversion, the monomer concentration in aqueous phase is low, so that the aqueous phase radicals take longer times to reach the length z to become able to entry into particles, thus favoring the aqueous phase termination to occur. Consequently, not all oligomeric radicals formed from the initiator decomposition and aqueous-phase propagation will enter into polymer particles thus diminishing the initiation efficiency. Therefore, the number of radicals that enter into particles is smaller than the amount of radicals formed in the aqueous phase by thermal decomposition of initiator.

In Figure 2b, it can be noted that the concentration of initiator in the aqueous phase follows a behavior similar to that of the initiator solution feed stream and does not show strong differences between the reactions.

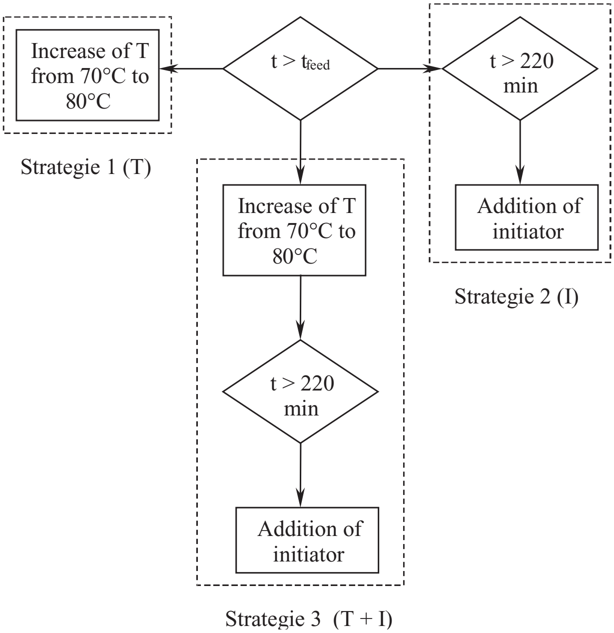


Figure 1.
Strategies of residual monomer reduction implemented before time feed (t_{feed}).

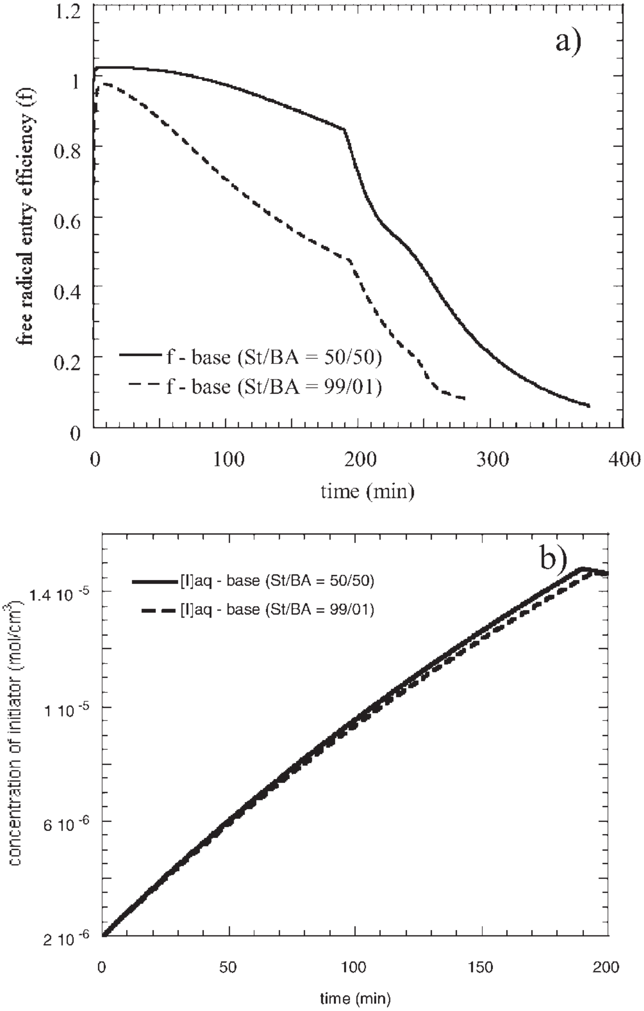


Figure 2.

a) Evolution of initiation efficiency during feeding time for base reactions with St/BA ratio equal 50/50 and 99/01; and b) Initiator concentration in the aqueous phase during feeding time for base reactions with St/BA ratios equal to 50/50 and 99/01.

The behavior of free radical entry efficiency for different strategies of residual monomer content reduction is presented in Figure 3. For the sake of brevity, Figures 3 only shows the results for Sty/BA ratio equal 99/01, however, results for St/BA equal 50/50 follow similar trends. The results of the simulations in Figure 3 show a significant decrease of radical entry efficiency in the end of the monomer feed time. This decrease occurs because the radicals in the aqueous phase will take longer times to reach the size z in order to be able to enter into a particle, thus favoring the occurrence of termination in the aqueous phase. Besides it is important to point out that at higher temperature applied at the end of the polymerization, the entry efficiency is further reduced because termination is favored due to the increase in aqueous phase diffusion of the radicals.

Figures 4 and 5 show the variation of total radical concentration in aqueous phase, with and without considering the

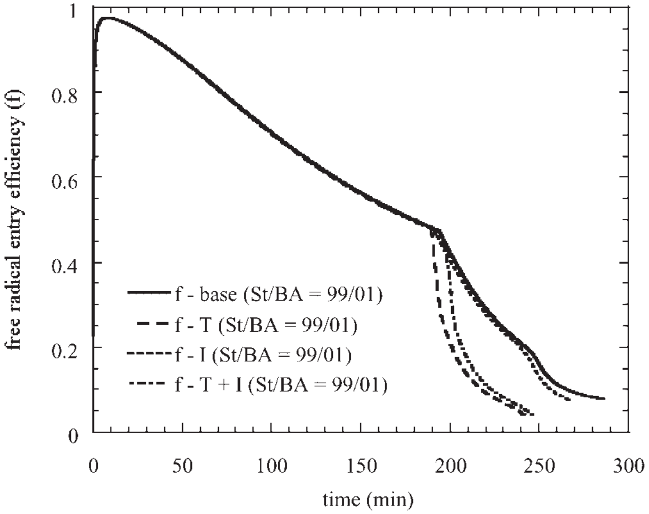


Figure 3.
Behavior of free radical entry efficiency and the effect of different strategies of residual monomer content reduction for reactions with St/BA ratio equal 99/01.

kinetics of termination in the aqueous phase, respectively. It can be noted that the concentration of radicals in the aqueous phase is slightly higher when the aqueous phase kinetics are not considered.

In addition, reactions with 50% St showed higher concentrations of radicals in the aqueous phase than reactions with 99% St. This may be attributed to the higher solubility of BA in water (0.2 g/100 g water)[26] than that of St (0.03 g/100 g water).[26]

In Figure 4, when the kinetics of termination in the aqueous phase was taken into account, it can also be noted that in reactions with 50% St the concentration of radicals ($[R_T^{ent}]_{aq}$) increase during the whole monomer and initiator feeding time. On the other hand, the reactions with 99% St show a maximum in concentration of radicals during the monomer and initiator feeding time (around 100 minutes) after which $[R_T^{ent}]_{aq}$ starts to decrease slightly. This early decrease is due to the low solubility of St in the aqueous phase, consequently, radicals enter "faster" into particles.

Figures 4 and 5 show that the increase in temperature (strategies 1 and 3) causes an increase in the radical concentration in the aqueous phase, due to the acceleration of initiator decomposition. This effect is noted even without further initiator addition (strategy 1). On the other hand, reactions where the initiator was fed and the temperature was maintained constant (strategy 2) do not show a significant increase in the total concentration of radicals in the aqueous phase.

In Figure 4 it can also be noted that the use of temperature increase (strategies 1 and 3) causes significantly lower radical concentrations at the final minutes for the reactions with St/BA ratio 50/50 (Figure 4a) than for the reactions with St/BA ratio 99/01 (Figure 4b). Under this condition, monomer concentration in small, and consequently, the radicals in aqueous phase take longer times to reach the length z to be able to enter into a particle, as mentioned previously. Besides, the increase of temperature may favor the termination between two radicals.

Figures 6 and 7 compare the evolution of monomer contents predicted by model and those measured by gas chromatography for base-case reactions and for reactions with residual monomer reduction strategies, with St/BA ratios equal to 50/50 and 99/01, respectively. As all reactions follow the

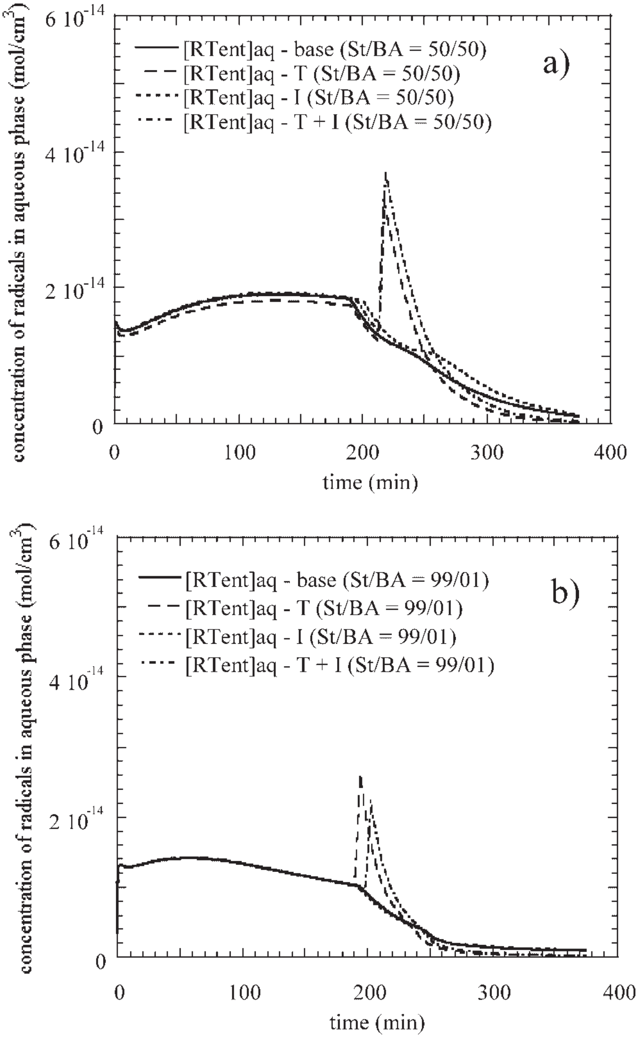


Figure 4.
Evolution of radical concentration in the aqueous phase ($[R_T^{ent}]_{aq}$) considering the kinetics of termination in aqueous phase for reactions with a) St/BA ratio equal 50/50; and b) St/BA ratio equal 99/01.

same formulation described in Table 2 during the monomer and initiator feed (i.e., before t=180 minutes), the behavior in this period is the same; therefore, the results are only presented for the period after 180 minutes of reaction, when the different strategies for monomer content reduction were applied.

Figures 6 and 7 show that the increase of temperature from 70 °C to 80 °C (strategy 1) seems much more effective in reducing the residual monomer content than the base reaction without change in temperature. At higher temperature, the diffusion of reactants is faster (both in aqueous phase and inside the particles) and the system is less prone to glass effect (if present). Also, higher temperature causes an increase in the initiator decomposition rate, consequently, increasing radical concentration (Figure 4) both in the aqueous phase and inside the particles.

On the other hand, the feeding of more initiator (strategy 2) shows much less

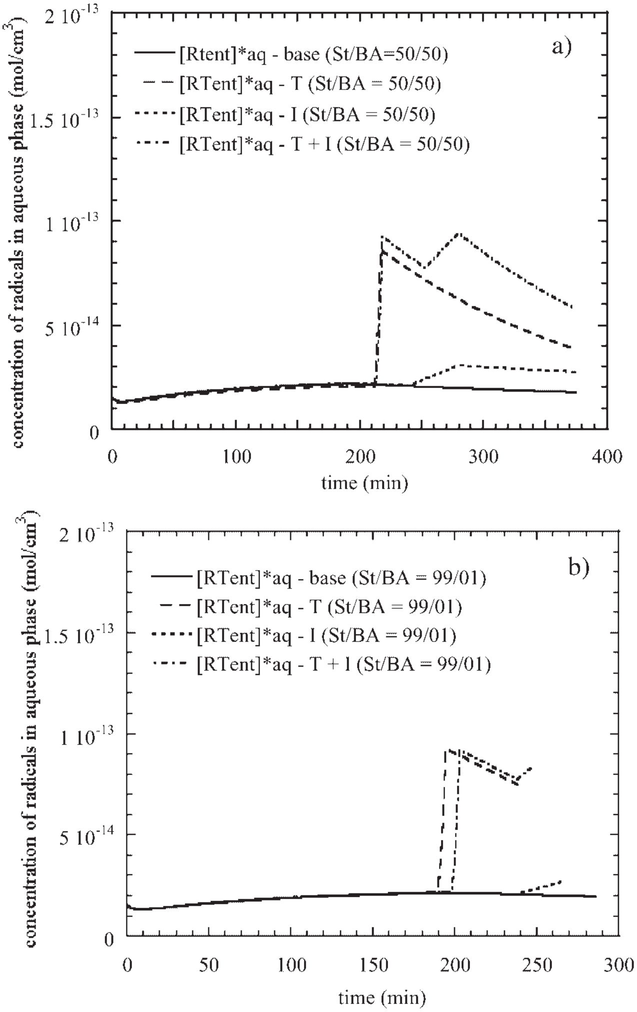


Figure 5.
Evolution of radical concentration in aqueous phase ($[R_T^{ent}]_{aq}^*$) without considering the kinetics of termination in aqueous phase for reactions with a) St/BA ratio equal 50/50; and b) St/BA ratio equal 99/01.

effectiveness in reducing residual monomer contents in comparison with temperature increase. The reduction in residual monomer using more initiator is equal or, surprisingly, sometimes worse than the corresponding base-case reaction. The continuous addition of more initiator increases only the concentration of radicals in aqueous phase, while most of monomer is located inside of the particles. Besides, the continuous addition of more initiator at constant temperature does not cause significant increase in radical concentration in the aqueous phase and in the polymer particles; oppositely, this may favor the termination reactions in aqueous phase and the consequent reduction in the initiation efficiency, as discussed before.

When both strategies were combined (temperature increase and addition of initiator, strategy 3), the residual styrene and butyl acrylate content reached approximately the same levels obtained in the reactions with only the temperature increase (strategy 1) or, in some cases, a little worse. The behavior is similar to those observed in

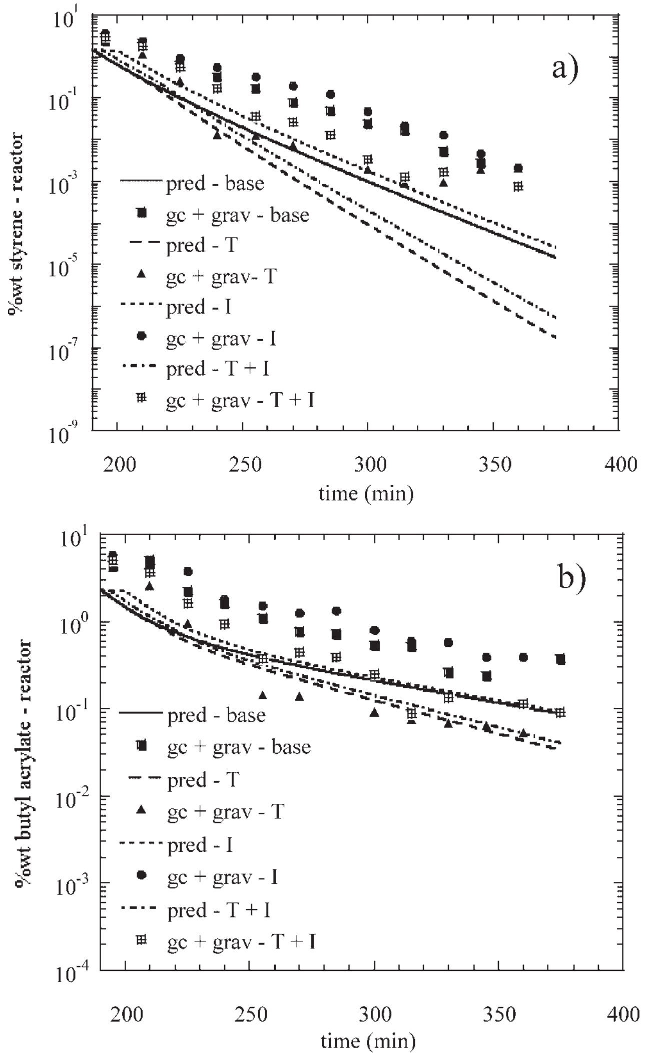


Figure 6.

Evolution of a) residual styrene content; and b) residual butyl acrylate content during final minutes of reactions for reactions with St/BA ratio equal 50/50.

the comparison of the effect of strategy 2 and the base case reaction, and the reasons are analogous to those discussed in the previous paragraph.

Worsen on residual monomer depletion caused by the addition of more initiator seems to be more perceptible for St/BA ratio 50/50 (Figure 6) than for St/BA ratio 99/01 (Figure 7). This can be related to the lower entry efficiency in systems with higher proportion of more water-soluble monomer BA.

Model predictions follow quite well the qualitative behavior observed for the experimental data, in special the relative intensity or effectiveness of each strategy of post-polymerization studied for the reduction of the residual monomer content. The entry efficiency may be also indirectly affected by radical anchoring at the particle

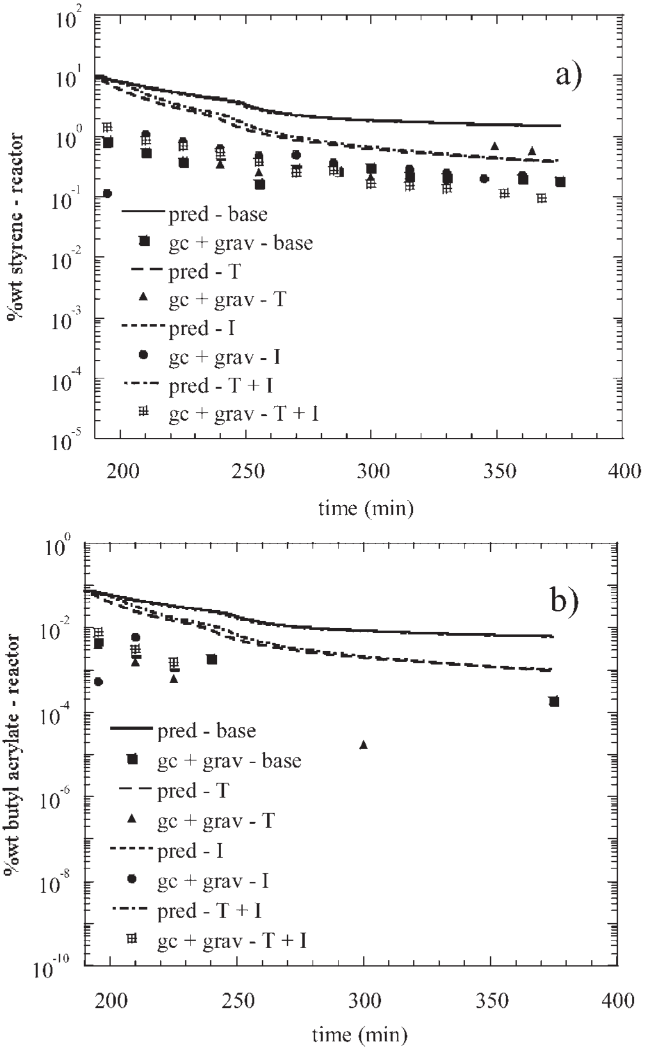


Figure 7.
Evolution of a) residual styrene content; and b) residual butyl acrylate content during final minutes of reactions for reactions with St/BA ratio equal 99/01.

surface, preventing them from reaching the monomer at the innermost parts of the polymer particle.[27]. The radical anchoring is not considered in the model and, therefore, can contribute to the deviations observed between the residual monomer content obtained by gas chromatography and the simulation results. Nonetheless, some level of experimental error also cannot be completely discarded at this range of very low concentrations. Quantitative agreement between model and experimental data in Figures 6 and 7 could be improved a little if the predictions at time $t = 180$ minutes (the "initial" time in Figures 6 and 7) were reallocated to the experimental value (i.e., most part of the observed mismatch originates from the deviations of model predictions in the previous period, $t < 180$ minutes).

Conclusion

The influence of aqueous phase kinetics on the residual monomer content and on the performance of selected residual monomer reduction strategies was verified both experimentally and through model predictions. The results showed significant decrease of entry efficiency during the monomer feeding period that diminish the concentration of radicals in aqueous phase that may enter into the polymer particles, thus reducing the average number of radicals per particle. The results showed that the initiation (entry) efficiency depends on the minimum length for a radical to enter into polymer particle, hence on the monomer solubility in aqueous phase. Experimental results indicate that residual monomer content can be effectively reduced by rising temperature at the post-polymerization period; however, the addition of more initiator (KPS) is not effective as a residual monomer strategy. A model that accounts for the reduction of initiator efficiency (radical entry efficiency) was successfully used to explain the experimental observations and was able to correctly predict the qualitative trends of the performance of different residual monomer reduction strategies.

Acknowledgements: The financial support from FAPESP - Fundação de Amparo à Pesquisa do Estado de São Paulo, CNPq - Conselho Nacional de Desenvolvimento Científico e Tecnológico and CAPES – Coordenação de Aperfeiçoamento de Pessoal de Nível Superior is gratefully appreciated. The authors also thank CIBA Specialty Chemicals and BASF for providing monomers and Beatriz Cassens, Marcos Diego P. Santana; Natália Carvalho Silva, Rafael Paradella de Oliveira for their assistance during the reactions.

[1] P. H. H. Araújo, C. Sayer, J. G. R. Poço, R. Giudici, *Polym. Eng. Sci.* **2002**, *42*, 1442.
[2] B. S. Casey, B. R. Morrison, R. G. Gilbert, *Prog. Polym. Sci.* **1993**, *18*, 1041.
[3] I. A. Maxwell, B. R. Morrison, D. H. Napper, R. G. Gilbert, *Macromolecules* **1991**, *24*, 1629.
[4] K. Y. van Berkel, G. T. Russell, R. G. Gilbert, *Macromolecules* **2003**, *36*, 3921.
[5] A. Keramopoulos, C. Kiparissides, *Macromolecules* **2002**, *35*, 4155.
[6] P. H. H. Araújo, R. Giudici, *Comp. Chem. Eng.* **2003**, *27*, 1345, **2004**, *28*, 575.
[7] W. H. Hirota, P. H. H. de Araújo, R. Giudici, C. Sayer, in proceedings of *2nd Mercosur Congress on Chemical Engineering/4th Mercosur Congress on Process Systems Engineering*, **2005**, Rio de Janeiro, Brazil.
[8] R. G. Gilbert. **1995**. *Emulsion Polymerization: A Mechanistic Approach*, 1° Ed., Academic Press, London, San Diego.
[9] J. Ugelstad, P. C. Moek, J. O. Aasen, *Journal of Polymer Science* **1967**, *5*, 2281.
[10] S. Omi, K. Kushibiki, M. Negishi, M. Iso, *Zairyo Gijutsu* **1985**, *3*, 426.
[11] J. S. Ventras, J. L. Duda, *J. Pol. Sci.: Pol. Phys.* **1977**, *15*, 403.
[12] C. Plessis, G. Arzamendi, J. R. Leiza, H. A. S. Schoonbrood, D. Charmot, J. M. Asua, *Macromolecules* **2002**, *33*, 4.
[13] A. Penlidis, Polymer Reactor Design, Optimization and Control in Latex Production Technology. 1986. Ph.D. Thesis - McMaster University. Canadá, **1986**.
[14] J. Gao, A. A. Penlidis, *J. Macromol. Sci. – Rev. Macromol. Chem. Phys.* **1996**, *C36*, 199.
[15] C. Plessis, G. Arzamendi, J. M. Alberdi, A. M. van Herkel, J. R. Leiza, J. M. Asua, *Macromol. Rapid Commun.* **2003**, *24*, 173.
[16] D. A. Paquet, W. H. Ray, *AIChE J.* **1994**, *40*, 73.
[17] T. F. McKenna, C. Graillat, J. Guillot, *Polymer Bulletin* **1995**, *.34*, 36.
[18] E. Ginsburger, F. Pla, C. Fonteix, S. Hoppe, S. Massebeuf, P. Hobbes, P. Swaels, *Chemical Engineering Science* **2003**, *58*, 4493.
[19] J. Brandrup, E. A. Immergut, *Polymer Handbook*. 3rd ed. New York: Wiley, 1989.
[20] L. M. Gugliotta, G. Arzamendi, J. M. Asua, *Journal of Applied Polymer Science* **1995**, *55*, 1017.
[21] N. Tefera, G. Weickert, K. R. Westerterp, *J. Appl. Pol. Sci.* **1997**, *63*, 1663.
[22] I. Barudio, G. Févotte, T. F. McKenna, *European Polymer Journal* **1999**, *35*, 775.
[23] A. Echevarría, J. R. Leiza, J. C. de La Cal, J. M. Asua, *AIChE J.* **1998**, *44*, 1667.
[24] K. Y. van Berkel, G. T. Russell, R. G. Gilbert, *Macromolecules* **2003**, *36*, 3921.
[25] R. A. M. Vieira, MSc. Thesis **2000**, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil.
[26] K. W. Min, W. H. Ray, *J. Macromol. Sci., Revs. Macromol. Chem.* **1974**, *C11*(2), 177.
[27] J. I. Amalvy, J. M. Asua, C. A. P. Leite, F. Galembeck, *Polymer* **2001**, *42*, 2479.