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Emulsion Terpolymerization of *St/MMA/Bua*: III. Modeling of Bua Backbiting, Diffusion of Monomers and Polymers in the Particle, and Bua Induced Branching

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EMULSION TERPOLYMERIZATION OF ST/MMA/BUA MODELING OF BUA BACKBITING AND DIFFUSION OF MONOMERS AND POLYMERS IN THE PARTICLE AND BUA INDUCED BRANCHING

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Abstract- In this work, the BuA backbiting and its k_p -gel effect is included in a previous published model for the simulation of the emulsion terpolymerization of *St/MMA/BuA*. It is then possible to evaluate the branching of this terpolymer and the average diffusion of the monomers, polymers and polymer radicals. The diffusion is evaluated through the propagation and termination coefficients with a modification of the Schmoluchowski equation. On the other hand, it is also found that the BuA propagation coefficient depends on the fraction of BuA free volume $X_{v,BuA}$ in the terpolymer and that the kind of model suitable for the simulation of the k_p -gel effect is determined by the rate of polymerization R_p , the number of radicals in the particle per mol of monomers $\#R/n$ and the total diffusion of the polymer radicals in the particle $n_T D^{PR}$.

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1. INTRODUCTION

The copolymers of butyl acrylate BuA synthesized by emulsion polymerization are important as resins for the paint industry [1,2]. In particular, the increment of the branching of their chains promotes a lower swelling of the BuA copolymer by the solvent [3]. The branching also avoids the easier dispersion of carbon black [4]. Both effects modify the characteristics of the paint with technological and economical consequences. The branching is estimated through the branching density BD, to say, the fraction of branched BuA monomer units to the total number of monomer units polymerized [3].

The branching in a polymer with BuA is mostly caused by the backbiting reaction of BuA (intramolecular polymer chain transfer). The backbiting reaction is substantially carried out through a ring of six carbon atoms (abstraction 1:5), when the BuA ended secondary radical finds a BuA unit in the pen-penultimate position and abstracts the hydrogen of the tertiary carbon near to the carbonyl group (See Supporting Information Section S-1) [5,6]. This

abstraction of hydrogen forms a lower reactive tertiary electrophilic radical [7]. We emphasize the word electrophilic because the tertiary radical is joined to the carbonyl group of the butyl acrylate, which attracts the charge of the tertiary radical and increases its electrophilicity. This tertiary radical propagates with a branch of two inactive monomers. The penultimate effect is present in the backbiting reaction of the terpolymer of styrene/methyl methacrylate/butyl acrylate *St/MMA/BuA* because the presence of penultimate monomers of *St* or *MMA* decreases the backbiting reaction as a consequence of steric effects [5]. At low temperatures $T < 80^\circ\text{C}$, as it happens in the emulsion polymerization of *St/MMA/BuA*, the β -scission [3,8] and depropagation side reactions are negligible and they are not taken into account in the modeling of its backbiting.

A lower concentration of monomer leads to a higher degree of branching due to a higher proportion of intramolecular (backbiting) and intermolecular polymer chain transfer with respect to the propagation reaction [3]. For this reason, it is expected a higher proportion of branching in the semicontinuous processes. Besides, it has been found that a higher amount of chain transfer agent reduces the backbiting reaction in acrylics, and correspondingly their branching. There are three explanations to this phenomenon: 1. Transfer of the proton (in the case of thiols) or of the halogen (patching in the case of halogenides) to turn off the reactivity of the tertiary electrophilic radicals; 2. The chain transfer agent decreases the chain length of the polymer chain and there are lesser active sites for the radical intramolecular chain transfer to the polymer; 3. The decrement of the degree of polymerization induced by the transfer agent provokes a diminution of the value of the kinetic coefficients of BuA. This is the hypothesis of kinetic coefficients depending of the degree of polymerization. On this way, a lower value of the kinetic coefficients of BuA induces a higher lessening of the BuA backbiting kinetic coefficients and, in consequence, a decrement of the branch density BD. In the case of bulk polymerization, Agirre et al. [3] discarded the patching of the tertiary electrophilic radicals because the signals in MALDI-TOF and NMR spectra for the

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patched carbon were not found. Nevertheless, Ballard reported that a more careful analysis of the spectra indicates a signal related to the patching of these radicals. Ballard also found that the incertitude of the temperature in bulk polymerization does not allow determining the precise magnitude of the patching by the transfer agent [9]. In the case of solution polymerization, Ballard concluded through the fitting of computer simulations to the experimental data that the 1st hypothesis is discarded. This is due to a low value of the kinetic rate of the chain transfer agent which is not enough to avoid the backbiting of BuA. By the contraire, chains with a lesser degree of polymerization decrease the branching of the polymer. These calculations validate then the 2nd hypothesis. On the other hand, Ballard also concluded that the 3th hypothesis is not valid because the kinetic rate in degrees of polymerization greater than 3 does not appreciably depend on the degree of polymerization or the chain transfer agent CBr₄ [9]. On the other hand, there are additional kinetic rates in the emulsion polymerization in comparison to the bulk and the solution polymerization: kinetic rate of radical desorption from the particle to the aqueous phase R_i and kinetic rate of capture of radicals from the water phase into the particle R_a . So, the concentration of BuA monomeric radicals in the particles is influenced by their capture/desorption into/from the particles and then the backbiting and consequently the branching are influenced by these phenomena. Besides, the influence of the surface on the kinetic rates and the concomitant hypothesis of homogeneous reaction throughout the particle must be evaluated because the emulsion polymerization is compartmentalized in particles emulsified in water. The correct assessment of surface dependence of the radicals desorption from the particle, for example, helps to determine more accurately the branching of the St/MMA/BuA terpolymer.

The homogeneous reaction throughout the particle was first postulated by Harkins [10,11], but the presence of domains such as a core shell structure in the particle can influence the balance of polymer radicals. On this way, it has been found that the reaction on the surface influences the desorption rate of monomeric radicals R_i . This is the case when the backbiting reaction of BuA is taken into account to simulate the molecular weight of the terpolymer [12]. The influence of the surface on the balance of radicals has been found out in particles of 250 nm for PMMA at high conversions, but not in particles of 25 nm [13]. For this reason, it is necessary to determine if the other kinetic rates are surface dependent in the emulsion terpolymerization of St/MMA/BuA. The verification must be done in processes in which the consideration of polymerization in all the volume or on the surface modifies appreciably the outputs of conversion and/or molecular weight. In our experimental setup the verification was done in batch B-3 in which the higher

amount of water soluble monomers led to a high desorption of the monomeric radicals from the surface:

This verification was also done in the seeded semicontinuous BS-1 in which the particle volume was high, see below. On the other hand, it has been found in the emulsion terpolymerization of St/MMA/BuA that the transfer to monomer R_m is not so important for the evaluation of the conversion and the molecular weight [12].

We consider that the evaluation of the k_p -gel effect in terpolymers in which the backbiting of BuA occurs is more sensitive for testing the hypothesis of homogeneous particle-phase polymerization. This is due to the high reactivity of BuA-ended secondary radicals ($k_{p, BuA0} = 32390 \text{ dm}^3/\text{mol/s}$ at 55 °C) and the low reactivity of the tertiary electrophilic radicals ($k_{p, BuAbb} = 34.45 \text{ dm}^3/\text{mol/s}$ at 55 °C) [5]. The gel effect in BuA causes a high variation of these propagation coefficients [12] and then the simulation model must be more exact in order to fit the outputs of conversion and molecular weight. On this way, the inclusion of the hypothesis of particle- phase polymerization must give outputs in accordance to the experimental results. In this context, the values of the diffusion of the monomers D^M and polymers D^P in the particle determined by the simulation model must also correspond to the values found in the literature. The behavior of these diffusion coefficients in the reaction can also help to understand the causes of the gel effect. It has been found that the diffusion of St in polystyrene PSt [14] is of the order of $10^{-6} \text{ cm}^2/\text{s}$ at $W_p = 0.5$ and $T = 50 \text{ °C}$. On the other hand, the diffusion of MMA in polymethylmethacrylate PMMA is of the order of $10^{-5} \text{ cm}^2/\text{s}$ [13] at $W_p = 0.5$ and $T = 50 \text{ °C}$. Furthermore, the diffusion of the monomers of BuA or MMA in a copolymer of MMA/BuA (20-80 wt%) is of the order of $10^{-7} \text{ cm}^2/\text{s}$ [15] at 50 °C and $W_p = 0.6$. For this reason, it is expected a similar trend in the terpolymer of St/MMA/BuA. In principle, the Rouse model can be applied to evaluate the diffusion of the polymers D^P in a concentration lower than the critical concentration for the overlap of the polymer chains c^* (concentration in which the polymers interpenetrate in the dilution regime). On this way, the Rouse model predicts a dependence of the polymer diffusion coefficient as $D^P \propto (N^P)^{-1}$ [16]. N^P is the degree of polymerization of the polymer and is obtained from the one and second moment of the molecular weight distribution of the dead polymer v_1 , v_2 , respectively. On the other side, in accordance to the reptation model the diffusion of the polymer D^P scales with N^P as $D^M/(N^P)^n$ [17,18] with $n = 2$ after the critical concentration for the entanglements c^{**} . Griffiths et al. have pointed out that the exponent should increase progressively from $n = 0.5 - 0.6$ at infinite dilution to $n = 2$ at a concentrated solution [19]. By their part, Tulig and Tirrell have emphasized, the dependence of the diffusion of the polymer D^P on the concentration of the polymer solution “c” with a

dependence of $c^{0.75}$ at $c < c^{**}$, and $c^{1.75}$ at $c > c^{**}$ in accordance to the reptation model [20-21].

In our previous work [12], we only reported the results of the simulation of the backbiting of the *BuA*-ended polymer radicals. The purpose of this work is to explain in more detail the previous results and correlate the backbiting to the diffusion and the branching phenomena in the emulsion terpolymerization. First, we describe the new equations added to the previous terpolymerization model as consequence of the *BuA*-ended secondary polymer radicals backbiting. As a general overview, we make a comparison of the outputs of conversion and glass transition temperature between the average k_p - k_t model for the terpolymerization developed in the previous work and the model which includes the backbiting of *BuA*. After that, we correlate the gel effect to the diffusion of monomers and polymer radicals in order to explain the causes of the gel effect. As a last part of this work, we make an analysis of the dependence of the branching of the terpolymer to the kinetic conditions of the emulsion terpolymerization. We consider that the key contribution of our work is the evaluation by first time of the diffusion of monomers in the particle. Also, our calculations differentiate the diffusion of the polymer radicals from the polymer molecules.

II. REVIEW OF THE EXPERIMENTAL DATA

The composition and conditions of batches B-1 to B-4, semicontinuous SC-1 to SC-4 and seeded semicontinuous BS-1 are given in our previous work. The batches B-1, B-2 and B-4 in addition to the semicontinuous SC-1, SC-2 and SC-3 have the same feed composition of *St/MMA/BuA* (25/50/25 wt%) near to the azeotropic unitary composition. The batch B-3 and the semicontinuous SC-4 have the feed same composition (17/33/50 wt%). The seeded semicontinuous BS-1 was near to composition of B-1 (29/45/26 wt%). The addition rate of monomers was: SC-1 (0.27 g/min), SC-2 (0.48 g/min), SC-3 (0.84 g/min), SC-4 (0.34 g/min), BS-1 (0.50 g/min). The reaction temperature was 55°C, at exception in B-4 and BS-1 in which the reaction temperature was 70°C [12]. The strategy of monomers addition and initial composition of the seed in seeded semicontinuous BS-1 tried to keep the proportion of the monomers in the terpolymer almost constant throughout the polymerization reaction. For that reason, the reaction of the batch used as seed was near the unitary azeotropic composition and was stopped at 77.5 % wt% of conversion in order to avoid a higher drift in the composition of the monomers in the terpolymer. This batch was then distilled at low pressure in order to discard the residual monomers. The conversion only increased to 79.2 wt% after the distillation. Most of the monomers in the emulsion were in the particles and the higher boiling point of the acrylic

monomers with respect to water produced their lower rate of distillation. So, in accordance to the mass balance, the water was the most distilled liquid and the proportion of monomers in the emulsion slightly increased from 3.2 to 4.1 wt%. On this way, from the 150 g of the distilled emulsion that was used as seed, the mass of monomers was 6.2 g as reported in the previous work [12]. In addition, the values of the final molecular weight for the processes are: B-1: $M_n = 45000$, $M_w = 102000$; B-2: $M_n = 31000$, $M_w = 57000$, B-3: $M_n = 34000$, $M_w = 52000$; SC-1: $M_n = 28000$, $M_w = 47000$; SC-2: $M_n = 34000$, $M_w = 65000$; SC-3: $M_n = 43000$, $M_w = 72000$; BS-1: $M_n = 98000$, $M_w = 299000$ g/mol [22-23].

We have made the simulation of the transition glass temperature T_g and DSC thermograms. We have verified its results with the experimental DSC thermograms obtained in a DuPont 4210 DSC. The experimental DSC thermograms were run from -70 °C to 130 °C with a temperature rate of 10°C/min at open panel with a flux of N_2 . The sample approximately weighted 10 mg. The simulation of the DSC was better for the batch processes and the variable that adjusted better the experimental range was ΔT_{gi} , as seen below (The equations for the simulation of T_{gi} and the DSC thermograms are given in Supporting Information Section S-6).

III. BACKBITING REACTION ADDED TO THE PREVIOUS TERPOLYMERIZATION MODEL

The simulation model for the emulsion terpolymerization given in the previous article [12] is extended to include the backbiting side reaction of *BuA*.

a) *BuA* Backbiting model considerations

- β -scission [8] and depropagation reactions are not considered.
- The total number of j-ended radicals is obtained by the Nomura's semiempirical equation for the radicals in the particle [24]. The *BuA*-ended tertiary electrophilic radicals have the same kinetic processes as the secondary *BuA*-ended radicals: propagation, termination, transfer to monomer and transfer to chain transfer agent, with exception of the rate of capture of radicals into the particle and rate of desorption. The last rate is not considered because the tertiary radicals have a degree of polymerization greater than 2 and then they are not desorbed.
- The k_p -gel effect of the *BuA*-ended radicals starts since the beginning of the reaction [12].
- The constants of the Hamielec model of k_p -gel effect are evaluated independently to the Ray and W_p models. The constants of the two last models are interrelated through our previous procedure [12].

- The model considers the initiation, termination and desorption of radicals in the aqueous phase in Equation (S-5) - (S-11) of Supplementary Information of the previous work [12]. The model does not consider the propagation of radicals in the aqueous phase. Through the evaluation of the experimental value of particle diameter vs conversion, the model includes the increment of the diameter by the homogeneous nucleation and the subsequent adsorption in the particle. In the previous work, the simulation of the diameter of the particle through the Langmuir adsorption curve includes the increment of the diameter by homogeneous nucleation through the adjustment of the value of the exponent x of the micellar nucleation. The exponent x is given in Table 4 of the previous work [12].

b) Materials Balance

The mass balance was the same as the previous model [12] splitting the term of BuA radicals in terms of secondary and tertiary radicals.

c) Average total number of j -ended radicals in the particle n_T

The total average number of j -ended radicals in the particle " n_T " was calculated through the semi-empirical equation of Nomura [24]. The equations for finding n_T only added the term of backbiting. In order to not be redundant with the previous work, these equations are given in Supporting Information Section S-1. The kinetic rates are also given in that section. The number of BuA-ended tertiary radicals n_{cbb} were calculated through a mass balance of the kinetic rates (#rad/part/s) of backbiting R_{ncbb} , propagation $R_{p,ncbb}$, termination $R_{t,ncbb}$, transfer to monomer $R_{m,ncbb}$ and transfer to chain transfer agent $R_{T,ncbb}$ in accordance to Table I. The probability $P_{ijk(i,j,k)}$ of existence of the j -ended radical triad ijk at time t was calculated by the product of the probabilities of the occurrence of the n_i , n_j , n_k -ended radicals (without considering the tertiary radicals of BuA) at times $t-3\Delta t$, $t-2\Delta t$ and $t-\Delta t$, respectively. Δt is the increment of time for the evaluation of the reaction kinetics, in this case 0.001 s. This procedure is different to the one of Wang and Hutchinson [5].

The total average number of j -ended radicals in the particle n_T and the average number of other radicals that the BuA- tertiary radicals " n " are given by:

$$n_T = n_a + n_b + n_c + n_{cbb} \quad (1a)$$

$$n = n_T - n_{cbb} \quad (1b)$$

With:

$$\text{If } n < 0 \text{ then } n_T = n_{cbb} \text{ and } n = 10^{-9} \quad (1c)$$

The simulation was also performed considering a proportional amount of the radicals n and n_{cbb} when $n_{cbb} > n_T$, but it did not give congruent results. The explanation of this behavior is that the formation of the tertiary BuA-ended radicals needs of the backbiting of polymer radical with a degree of polymerization at least of $j = 3$. For this reason, these radicals are not desorbed ($R_{ncbb} = 0$) because the model considers desorption of monomeric radicals with $j = 1$.

As a chemical kinetic ground, the high reactivity of the BuA secondary radicals and the corresponding lower reactivity of the tertiary BuA-ended radicals produce a lower amount of the secondary radicals in the particle, as will be seen below.

d) Reaction Kinetics

(The reason of defining the k_p -gel effect in this article is given in Supporting Information Section S.1.3.) The evaluation of the kinetic rates R_i , R_p , R_m and R_T depends on the propagation coefficient $k_{p,ij}$ (See Supporting Information, Tables S-1 and S-2), which has a k_p -gel effect. For this reason, we estimated first this variable and then we used it in the corresponding kinetic rates.

i. Propagation rate coefficient of radical " i " to monomer " j " $k_{p,ij}$

We have analyzed the k_p -gel effect for this system in the previous article [12]. In this work the backbiting of the BuA secondary-ended radicals was taken into account, in which the k_p -gel effect starts since the beginning of the reaction. The apparition of the k_p -gel effect in BuA is caused by the lower free volume V_f of St and MMA than of BuA in the terpolymer ($V_{f,PS} = 0.0025$, $V_{f,PMMA} = 0.0032$, $V_{f,PBuA} = 0.0605$ at 55°C for the homopolymers) [12]. In principle, we have kept the values and restrictions of the k_p -gel constants for St and MMA [12]. On the other hand, we have found the values of the constants for BuA for the V_f Ray's k_p -gel model in the batch process B-1 iterating at the same time with the values of concentration of monomers in the particle $[M]_p$ and critical value of free volume for BuA $V_{f,cc}$ as explained in the section Methodology below. Then, we have matched the equations of the V_f Ray's and W_p k_p -gel models for BuA-ended radicals in order to obtain the constants A_i and $V_{f,ci}$ for the W_p k_p -gel model [12]. The equating gave very different results in the case of BuA in the equating of V_f Ray's and the V_f Hamielec's k_p -gel models. Probably, the sensitivity of the BuA backbiting reaction for the abrupt change of the value of $k_{p,BuA}$ set up this discordance of the Hamielec's k_p -gel model because this model predicts a lower k_p -gel effect (Higher R_p) in the batch processes than the W_p and V_f Ray's models [12]. On this way, the constants of the Hamielec's k_p -gel model were calculated of independently manner.

It has been realized by Sundberg et al. [25] that the constant A_i of the exponential term for the

Hamielec's equation in the homopolymers for the propagation coefficient k_p is the critical free volume $V_{f_i}^{M,*}$ for the beginning of a monomer to jump:

$$\frac{k_p}{k_{p0}} = \exp\left[-A_1\left(\frac{1}{V_f} - \frac{1}{V_{f0}}\right)\right] \quad (2)$$

V_{f0} is the critical free volume for the beginning of the k_p -gel effect.

The values of the constants $A_{ij} = V_{f_i}^{j,*}$ in the emulsion terpolymerization of *St/MMA/BuA* were near to the free volume of the homopolymers times 6 (we consider the value of $A_{1,BuA}$ for backbiting, see Table 3): $A_{1,St} = V_{f_i}^{St,*} = 0.015 \approx 6 V_{f_i,PS} = 6 (0.0025)$, $A_{1,MMA} = V_{f_i}^{MMA,*} = 0.015 \approx 6 V_{f_i,PMMA} = 6 (0.0032)$, $A_{1,BuA} = V_{f_i}^{BuA,*} = 0.35 \approx 6 V_{f_i,BuA} = 6 (0.0605)$. These constants were found by iteration to fit the conversion curve [12] and the similarity is worthy, because it shows that free volume of the homopolymers is related to the k_p -gel effect. Consequently, a free volume V_f near to the j -ended radical of the terpolymer higher than 6 of the free volume of the average homopolymer " j " is necessary to do not have k_p -gel effect. We consider that the constants A_3 for the W_p model also have an equivalent meaning as in Equation (2).

It was observed a point of change of curvature of the rate of polymerization at $X_0 = 0.78$ ($V_{fc2} = 0.05$ corresponding to $W_{pc2} = 0.7945$ in B-1), which was associated to an increment of the k_p value for the radicals of BuA [12]. We have associated this critical value of V_{fc2} to a critical value of the proportion of BuA free volume in the terpolymer X_{vf} ($X_{vf2} = 0.84$ in B-1) for the beginning of the increment of the BuA propagation coefficient. Then, we have used the critical condition $X_{vf} > X_{vf2} = 0.84$ for all the emulsion polymerization processes in the V_f k_p -gel models. In the W_p k_p -gel model, we used the condition $W_{pc2} > 0.7945$. We consider that the increment of $k_{p,BuA}$ was due to a higher free volume of the last portion of the terpolymer with a BuA-ended radical with a high proportion of BuA monomers in the terpolymer nearer to this radical given by the condition $X_{vf} > X_{vf2} = 0.84$. We have associated the increment of the value of $k_{p,BuA}$ with a change of the value of the constants in the k_p -gel models, that is, from A_{1k} to A_{2k} (See Tables 2 and 3). The change of the value of the constants produces a jump in the value of $k_{p,BuA}$ with its subsequent decrement associated to the fall down of free volume V_f . On this way, this jump is associated to a catastrophic behavior in the value of $k_{p,BuA}$. This catastrophic behavior is found when one monomer has an extremely higher reactivity than the other monomers [26]. In this case, the segmental

diffusion of the monomer ended radical of BuA is fast at a higher proportion of BuA in the terpolymer and then it produces an abrupt increment of the reactivity. This increment of the value of $k_{p,BuA}$ is produced by the higher free volume of BuA than that of St or MMA in the terpolymer. With this argument we support the idea that the contribution of the segmental diffusion is important to the evaluation of the k_p -gel effect [27], which is included in the diffusion of the polymer radical through its reptation. On this way, the diffusion of the monomers in the bulk of the solution is not as important in the selection of the k_p -gel model as their diffusion near to the polymer radical, because near to the polymer the friction exponentially grows up [28], and their diffusion falls down in the same way.

In Table 2 are given the corresponding equations for the Hamielec ($k = 1$), Ray, ($k = 2$) and W_p ($k = 3$) models before and after the critical point for BuA, $X_{vf} > X_{vf2} = 0.84$, and in Table 3 are given the values of the corresponding constants. It is observed in the processes batch, semicontinuous and seeded processes a critical value of V_{fc1} (W_{pc1}) associated to the beginning of the reaction ($V_{fc1} = 0.14$ corresponding to $W_{pc1} = 0.1865$ in B-1). This value of V_{fc1} is near to the value of V_f for the monomer St. At exception of batch B-3, the point of change of curvature at $X_{vf2} > X_{vf2} = 0.84$, only changed the value of the constant of the k_p -gel effect A_{1k} to A_{2k} , ($k = 1, 2, 3$ are the k_p -gel models). However, the critical value of V_{fc1} of 0.14 (corresponding to $W_{pc1} = 0.1865$ in B-1) remained the same as observed in Table 2. We consider that the original critical value of V_f ($V_{fc1} = 0.14$, $W_{pc1} = 0.1865$) had influence over the gel effect throughout the reaction in almost all the processes.

In the case of the fitting of batch B-3 with a higher composition of BuA, it was necessary to put the value of $V_{fc2} = 0.052$ ($W_p = 0.7945$) instead of the value used before of $V_{fc1} = 0.14$ ($W_{pc1} = 0.1865$;) in the expression $(1/V_f - 1/V_{fc1})$ at $X_{vf} > 0.84$. Then, we applied Benyahia's procedure for the termination k_t -gel effect of BuA in order to write the expression of the k_p gel effect as seen in Tables 2 and 3 [29]. On this way, an increment of the proportion of BuA in the batch B-3 caused that the value of V_{fc2} in the point of change of curvature ($V_{fc2} = 0.052$ see Table 3, near to the free volume of the homopolymer PBuA, $V_{f,BuA} = 0.05$) had influence on the k_p -gel effect in batch B-3.

ii. Diffusion coefficients in the particle

The diffusion of the polymer without chemical reaction is given by Equation (3) [30].

$$D^P = 6 k_B T \left[\frac{(2 L_{pers} - b)}{b (N + 1)} \right]^2 \left[\frac{(1 + \cos(\tau))}{(1 - \cos(\tau))} \right]^2 \frac{1}{\xi_{seg} \sigma_{SH}} \quad (3a)$$

$$L_{per} = \frac{b}{(1 + \cos(\tau))} \quad (3b)$$

We consider the model of wormlike chain (reptation of the polymeric radical chain with N monomers). The bond length is b and the bond angle is τ , k_B is the Boltzman constant (erg/K), T is the temperature (K), L_{pers} is the persistence length (cm) which is higher for stiff polymers and the sequence is $L_{pers,St} (\approx 9.0 \times 10^{-8} \text{ cm}) > L_{pers,MMA} (6.9 \times 10^{-8} \text{ cm}) \approx L_{pers,BuA} (6.9 \times 10^{-8} \text{ cm})$ [30], σ_{SH} is the hindrance factor which indicates the steric hindrance to rotate with the following sequence: $\sigma_{SH,St} (2.2) > \sigma_{SH,BuA} \approx \sigma_{SH,MMA} (1.9)$. There is not certitude in the value of the steric hindrance of BuA because this parameter increases with the size of the short branches (probably near to 1.9, which is the value of the polybutylmethacrylate PBuMA). ξ_{seg} is the friction coefficient of the segment of the polymer, in this case the monomer in the terpolymer (g/s).

As also explained below, a higher proportion of BuA in the terpolymer allows a higher diffusion of the

polymer radicals and of the monomers. The lower value of the friction coefficient for the segment of BuA, $\xi_{seg, BuA}$ is caused by the branches of butyl and the two monomer branches induced by the backbiting of the secondary polymer radicals of BuA. On this way, Ferry pointed out that the branching decreases the friction coefficient [31]. In order to calculate the diffusion coefficients of the terpolymer, it was defined that the effective propagation coefficient $k_{p,Tot}$ with gel effect, has an independent contribution [32] (similar to a parallel electric circuit) of chemical reactivity and diffusion as expressed in Equation (4) [33-34]. Equation (4) is another way to express the dependence of the propagation coefficient on the diffusion phenomena (parallel expression) to the W_p and V_f Hamielec's and Ray's models given in Table 3. In the later models, the dependence is through the division of the chemical propagation rate coefficient between the corresponding coefficient which considers the diffusion (series expression).

$$\frac{1}{k_{p,Tot}} = \frac{1}{k_p^{chem}} + \frac{1}{k_p^{diff}} = \frac{1}{k_{p,Tot0}} + \frac{1}{k_p^{diff}} \quad (4)$$

Where $k_{p,Tot0}$ is the chemical propagation coefficient without gel effect ($\text{dm}^3/\text{mol}_{mon}/\text{s}$) and k_p^{diff} ($\text{dm}^3/\text{mol}_{mon}/\text{s}$) is the propagation coefficient which depends on the diffusion of the monomer D^M near the polymer radical and the reactivity the polymer radical D^{PR} . If we consider that the diffusion of a polymer radical D^{PR} (cm^2/s) is given by the diffusion of its center of mass (com) $D^{com,PR}$ [18] with a translation by reptation [17] and by the reaction diffusion induced by the propagation of the j -ended radicals $D^{rd} = D^{rd,PR}$ (also named roving head diffusion or residual termination [35]). We could calculate the diffusion coefficients through the sequence of the calculations given in Table 4. This sequence was

established through a dimensional analysis of the Schmoluchowski equation for reaction of two species in accordance to Mills et al. [13], Russell et al. [35] and Stubbs et al. [18], which gives the equations given below (the corresponding deduction is given in Supporting Information Section S-2). It is important to remark that from the Schmoluchowski equation we obtained an expression specific for emulsion polymerization and, on this way, we could calculate the diffusion of the monomers D^M by using the propagation coefficients k_p^{diff} , $k_{p,Tot}$, $k_{p,Tot0}$, where k_p^{diff} is given by:

$$k_p^{diff} = k_p^{rd} + k_p^M \quad (5a)$$

$$k_p^{rd} = 4 \pi \frac{n_T}{[M_T]_p v_p} D^{rd} \left(\frac{\sigma_{LJ}^R}{2} + \frac{\sigma_{LJ}^M}{2} \right) = 4 \pi \frac{\#R}{1000 n} D^{rd} \left(\frac{\sigma_{LJ}^R}{2} + \frac{\sigma_{LJ}^M}{2} \right) \quad (5b)$$

$$k_p^M = 4 \pi \frac{n_T}{[M_T]_p v_p} D^M \left(\frac{\sigma_{LJ}^M}{2} + \frac{\sigma_{LJ}^R}{2} \right) = 4 \pi \frac{\#R}{1000 n} D^M \left(\frac{\sigma_{LJ}^M}{2} + \frac{\sigma_{LJ}^R}{2} \right) \quad (5c)$$

Where $k_p^{rd} = k_p^{rd,PR}$ is the propagation coefficient dependent on the reaction diffusion of the polymer radical and k_p^M is the propagation coefficient dependent on the diffusion of the monomer.

We have considered that the number of radicals R which reacts per mol of monomers $\#R/n$ (radicals/mol) is:

$$\frac{\#R}{n} = \frac{\#M}{n} = \frac{1000 n_T N_p V_w}{[M_T]_p v_p N_p V_w} = \frac{1000 n_T}{[M_T]_p v_p} \quad (5d)$$

We have used $\#R/n$ instead of N_A , the Avogadro's number, because the last variable corresponds to a mol of radicals, but in emulsion polymerization the number of j -ended radicals in the

particle is n_T , which reacts with the same number of monomers in reaction of first order per mol of monomers. Commonly $n_T < 0.5$, and for example in the simulation of B-1, there were 6.9×10^6 molecules of monomer in the particle for one j-ended radical at $X_0 = 99$ wt%. In this context, Chern and Poehlein have shown that the monomers are distributed homogeneously throughout the particle and in consequence there is not a gradient of concentration of monomers in the particle [36].

The frequency of jumping of the reaction diffusion coefficient D^d is given by $k_{p,Tot} [M_T]_p$ (1/s) [37]. The square of the average radius of gyration of the polymer radical divided by the number of monomers $a_{PR}^2/6$ (see Table 4) indicates how much the polymer has diffused from its center of gravity by each reaction of the polymer radical with the monomers.

Ferry [31] and Sundberg et al. [25] have analyzed the influence of the free volume in the diffusion of the polymers and monomers with the corresponding critical point in order to change the diffusion values of k_p . These authors indicate that a higher free volume V_f of the polymer solution allows a higher diffusion of the polymer radical and monomers. This is concluded in the following equation for the wormlike chain in the case of the diffusion of a polymer radical depending on the free volume V_f [25,30-31].

$$D^{PR} = \phi_{0,seg} N b^2 (2 L_{pers} - b) \exp(-V_f^{Seg,*}/V_f) \quad (6)$$

From the equations in Table 4, it can be observed that the diffusion of the monomer D^M near the polymer radical depends directly on the volume of the particle v_p , the concentration of monomers in the particle $[M_T]_p$ and inversely on the number of radicals in the particle n_T . The dependence of D^M on the free volume is through the gel effect implicit in $k_{p,Tot}$. On this way, using the Equation (4), (5a)-(5c)) with the Hamielec and W_p formulas for the gel effect:

$$D^M = \frac{k_p^{diff} [M_i]_p v_p}{4 \pi n_T \left(\frac{\sigma_{LJ}^M}{2} + \frac{\sigma_{LJ}^R}{2} \right)} - D^{rd} \quad (7a)$$

Vg.: Hamielec's model:

$$k_p^{diff} = \frac{k_{p,ji0}}{\left(\exp[A_{1j} \left(\frac{1}{V_f} - \frac{1}{V_{f0j}} \right)] - 1 \right)} \quad (7b)$$

W_p model:

$$k_p^{diff} = \frac{k_{p,ji0}}{\left(\exp[A_{3j} (W_p - W_{p0j})] - 1 \right)} \quad (7c)$$

As it will be shown below, D^{rd} was negligible. In Equation (7c) is shown the dependence of D^M to W_p .

In an analogous way, the termination coefficient $k_{t,Tot}$ has an independent (parallel expression) contribution of chemical reactivity and diffusion [33-34].

$$\frac{1}{k_{t,Tot}} = \frac{1}{k_t^{chem}} + \frac{1}{k_t^{diff}} = \frac{1}{k_{t,Tot0}} + \frac{1}{k_t^{diff}} \quad (8a)$$

With the expression of the Schmoluchowski equation for k_t^{diff} [38]:

$$k_t^{diff} = 4 \pi N_A 2 D^{PR,t} \left(\frac{\sigma_{LJ}^R}{2} + \frac{\sigma_{LJ}^R}{2} \right) \quad (8b)$$

We have used the following conditions for the evaluation the diffusion of the polymer radical in the termination process $D^{PR,t}$:

$$\text{Condition 0: } D^{PR,t} = \frac{D^M}{(N^{PR,t})^{n_0}} + D^{rd} \quad \text{for } c < c^* \text{ and } N^p < N^{**} \quad (9i)$$

$$\text{Condition 1: } D^{PR,t} = \frac{D^M}{(N^{PR,t})^{n_1} c^{n_3}} + D^{rd} \quad \text{for } c^* < c < c^{**} \text{ and } N^p < N^{**} \quad (9ii)$$

$$\text{Condition 2: } D^{PR,t} = \frac{D^M}{(N^{PR,t})^{n_2} c^{n_4}} + D^{rd} \quad \text{for } c > c^{**} \text{ and } N^p < N^{**} \quad (9iii)$$

$$\text{Condition 3: } D^{PR,t} = \frac{D^M}{(N^{PR,t})^{n_2} c^{n_3}} + D^{rd} \quad \text{for } c < c^{**} \text{ and } N^p > N^{**} \quad (9iv)$$

$$\text{Condition 4: } D^{PR,t} = \frac{D^M}{(N^{PR,t})^{n_2} c^{n_4}} + D^{rd} \quad \text{for } c > c^{**} \text{ and } N^p > N^{**} \quad (9v)$$

Specifically $D^{PR,t}$ is the diffusion coefficient (cm^2/s) of the polymer radical associated to the degree of polymerization of the radicals associated to termination $N^{PR,t}$, "c" is the concentration of polymer in the solution (g/cm^3). n_3 and n_4 are the exponents of the dependence of the diffusion coefficients $D^{PR,t}$ on the concentration "c". The concentration at the beginning of the overlap of the polymers c^* , in which the polymers interpenetrate, was calculated in accordance to Brown and Zhou [39] and given in Table 4. In the reptation model, $n_3 = 0.75$ and $n_4 = 1.75$ [17,20]. We consider that the diffusion of the monomers D^M takes into account the contribution of the critical concentration for the entanglements c^{**} and the critical value of

entanglement N^{**} for this reason they are not present in Equation (9ii) – (9v). The critical concentration c^{**} for the apparition of entanglements was found by the relation $c^{**} = K_c / N^{0.65}$. K_c was given by data of Tulig and Tirrell [20] The exponent 0.65 was calculated by the values of $c^{**} = 0.24 \text{ g/cm}^3$ and $M_n = 79,000 \text{ g/mol}$ of

PMMA reported by the last authors. This correlation was also validated for the data of Callaghan and Pinder [40] and Elias [30] for PSt. In fact, Tulig and Tirrell affirmed that the exponent is between 0.5 and 1 [20]. Then, we have evaluated Equation (9i)-(9v) solving for $N^{PR,t}$, V_g . For condition 2 in B-1:

$$N^{PR,t} = \left(\frac{D^M}{\left[\frac{1000 k_t^{diff}}{8 \pi N_A \left(\frac{\sigma_{LJ}^R}{2} + \frac{\sigma_{LJ}^R}{2} \right)} - D^{rd} \right] c^{n_i}} \right)^{(1/n_j)}$$

$$n_i = n_3 = 0.75, n_j = n_2 = 1.59 \quad (10)$$

The exponents n_0 , n_1 and n_2 , were varied in order to fit $N^{PR,t}$ the degree of polymerization of the polymer radicals N^{PR} deduced by the radical moments μ_0 , μ_1 as seen in Fig. 1. In the semicontinuous processes SC-3 and SC-1, N^{PR} was more higher than $N^{PR,t}$. This is explained by the hypothesis that the short chains are more important in the termination step as Russell has demonstrated by a balance of radicals [41]. We consider that in the semicontinuous processes, the real distribution of $N^{PR,t}$ was between the distribution of N^{PR} at the end of the addition of the monomers, N^{PR}_{max} , and the distribution which considers $n = 2$ given by de Gennes, N^{PR}_{min} .

The exponents found by this method were congruent with the fact that for a higher value of W_p corresponds a higher value of the exponent n_i . The sequence of exponents allowed explaining that a lower addition rate of the monomers leads to a lesser diffusion of the polymer radicals, as observed in Table 5. On this way, in the semicontinuous process SC-1 with lowest addition rate of monomers (more effect of diffusion of polymer radicals in the particle), the exponent n_2 , associated to the increment of concentration of the polymer, is the highest (1.85) for the same feed composition. Besides, in the process semicontinuous SC-3 with the higher addition rate of monomers, the exponent falls down to 1.70 (less effect of diffusion of polymer radicals in the particle), and in the batch process B-1 n_2 decreases to 1.59 (least effect of diffusion of polymer radicals in the particle). On the other hand, in the batch process B-3 with a higher proportion of BuA, the diffusion exponent n_2 increases to 1.7. Because the simulated different degrees of polymerization in the last two processes (Vg., $N^p = 242$ for B-1 and $N^p = 169$ for B-3 at $X_0 = 50 \text{ wt\%}$) and different composition of the terpolymer (Vg., St/MMA/BuA = 35/51/14 mol% for B-1 and St/MMA/BuA = 29/39/32 mol% for B-3 at $X_0 = 50 \text{ wt\%}$), the

dependence of the exponent of B-3 to N^p had a different trend. The final result was that the diffusion of the monomers, terpolymer and terpolymer radicals was higher in batch process B-3 (not shown) as it was expected by the low value of the PBuA's T_g , see below. On the other hand, it is worth to say that the value of the exponent n_0 , with a polymer concentration $c < c^*$, was selected as 1.4 in the batch process, value found for toluene or benzene in PSt at $W_p = 0.5$ [42]. The fitting to the experimental data was adequate with this value.

We have also performed the fitting with the addition of the critical value N^{**} , as Russell has proposed [41,43] and with or without the addition of the critical concentration c^{**} . On this way; $D^{PR,t} \propto (N^{PR,t})^{-n_0}$ for $N^{PR,t} < N^{**}$ and $c < c^*$ (Condition 0, see Equation (9)); $D^{PR,t} \propto (N^{PR,t})^{-n_1} c^{-n_3}$ for $N^{PR,t} < N^{**}$ and $c < c^{**}$ (Condition 1); $D^{PR,t} \propto (N^{PR,t})^{-n_2} c^{-n_4} (c^{**})^{-(n_3-n_4)}$ for $N^{PR,t} < N^{**}$ and $c > c^{**}$ (Condition 2), $D^{PR,t} \propto (N^{PR,t})^{-n_2} (N^{**})^{-(n_1-n_2)} c^{-n_3}$ $N > N^{**}$ and $c < c^{**}$ (Condition 3); and $D^{PR,t} \propto (N^{PR,t})^{-n_2} (N^{**})^{-(n_1-n_2)} c^{-n_4} (c^{**})^{-(n_3-n_4)}$ for $c > c^{**}$ and $N > N^{**}$ (Condition 4). (When we use the methodology of Russell without the normalized concentration c^{**} , it is written $c^{**} = 1$ in the later equations). We have found that the distribution of N^{PR} of the batch processes with Equation (9i)-(9v) was very similar to the distribution of N^{PR} found by the Russell's equations using c^{**} . The Russell's equations without c^{**} could not be evaluated in the batch processes, because the conditions 0, 1, 2 were present in almost all the reaction. On the other hand, the semicontinuous process helped to determine that the Equation (9i)-(9v) applied better to all the processes because the Russell equations with/without c^{**} gave higher value of N^{PR} at the end of the addition of the monomers (N^{PR}_{max}) and higher values of N^{PR} at intermediate conversion. Besides, the Russell expressions with c^{**} did not give the sequence that a lower addition rate of monomers implies a higher

exponent. For this reason, we did not use the Russell expressions.

Another method to evaluate the distribution of the number of polymer radicals was that proposed by Griffiths [19,44] in which the exponent of the polymer radicals is found by $n_i = 0.664 + 2.02 W_p$. However, the values of the exponents in the cases of batch processes were near to the value of $n = 2$, and when these values were used in the calculation of $N^{PR,t}$ (see Tables 4,5 and Fig. 1) the distribution was quite different to N^{PR} . For this reason, we did not use this approximation.

We have also considered the reptation model in which $n_1 = n_2 = 2$ [17]. We have found that k_t^{diff} calculated by Equation (8b) is much lower than the value given by the evaluation of Equation (8) with the values of $k_{p,Tot}$ and $k_{p,Tot0}$ found in the batch and semicontinuous processes. This kind of discrepancy was also found by Faldi et al. for the diffusion coefficients of the polymer radicals D^{PR} [45]. We consider that the exponents of the polymer radicals associated to the termination must be lower than 2 in order to have the same k_t^{diff} . The lower values are

$$\frac{k_p^M}{k_t^{diff}} = \frac{k_p^{diff}}{k_{t,Tot}} = \frac{\left(\frac{1}{k_{p,Tot}} - \frac{1}{k_{p,Tot0}} \right)}{k_{t,Tot}}$$

$$= \left(\frac{D^M}{D^{PR}} \right) \frac{1000 n_T}{N_A [M_T]_p v_p} = \left(\frac{D^M}{D^{PR}} \right) \left(\frac{\#R}{n} \right) \frac{1}{N_A} = (N^{PR})^{n_2} \left(\frac{\#R}{n} \right) \frac{1}{N_A} \quad (11b)$$

$$\frac{1}{k_{p,Tot}} = k_{t,Tot} (N^{PR})^{n_2} \left(\frac{\#R}{n} \right) \frac{1}{N_A} + \frac{1}{k_{p,Tot0}} \quad (11c)$$

Based on this last equation, we can explain the k_p -gel ($k_{p,Tot}$) effect through variables associated to propagation and termination phenomena.

IV. BRANCHING

The evaluation of the instantaneous branch density BD_i and the instantaneous branching fraction BF_i [9], and the corresponding averages of branching density BD [3] and branching fraction BF were done through the following equations.

$$BD_i = \frac{R_{p,cbb} \frac{N_p}{N_A}}{R_p} \quad (12a)$$

$$SBD = \sum_1^{niter} BD_i \quad (12b)$$

$$BD = \frac{SBD}{niter} \quad (12c)$$

indicative that the polymeric solution is not so concentrated. On the other hand, we have found that in accordance to the sequence of Table 4, the value of the diffusion of the polymer radicals associated to termination $D^{PR,t}$ is independent of the selection of the exponents n_0 , n_1 and n_2 . This is not the case for the values of the diffusion of the polymer radicals (obtained by the method of moments of the MWD) and dead polymers, D^{PR} and D^P , respectively. For the report of the values of $D^{PR,t}$ and D^P , we have used the values of the exponents n_0 , n_1 and n_2 of $N^{PR,t}_{max}$.

It is possible to find a relation between the total propagation coefficient $k_{p,Tot}$ and the total termination coefficient $k_{t,Tot}$. As seen later in Fig. 11 for the batch process B-1, $k^M \approx k_p^{diff}$, $k_{t,Tot} \approx k_t^{diff}$, and considering that $D^{rd} \approx 0$, $N^{PR} \approx N^{PR,t}$ (Fig. 1a) with $D^{PR} \approx D^{PR,t}$, $\sigma_{LJ}^R \approx \sigma_{LJ}^M$ and not effect of concentration "c" in the diffusion coefficient D^{PR} (Equation (9i)):

$$D^{PR} = \frac{1000 k_t^{diff}}{8 \pi N_A \left(\frac{\sigma_{LJ}^R}{2} + \frac{\sigma_{LJ}^M}{2} \right)} \quad (11)$$

$$BF_i = \frac{R_{p,cbb} \frac{N_p}{N_A}}{(R_{pc} + R_{p,cbb} \frac{N_p}{N_A})} \quad (12d)$$

$$SBD = \sum_1^{niter} BF_i \quad (13a)$$

$$BF = \frac{SBD}{niter} \quad (13b)$$

Where n_{iter} is the iteration number of the program. SBD and SBF are the accumulated branching density at n_{iter} iterations and the accumulated branching fraction at n_{iter} iterations, respectively.

V. METHODOLOGY

Most of the values of the variables found for the k_p - k_t average set of models [12] were used as a reference for the set of models which includes the backbiting of BuA. On this way, the values of the diameter of droplet D_d and correction factor F_c were the

same in order to compare the molecular weight results. Three Methods for evaluating the importance of the viscosity in the increment of $k_{p,BuA}$ at the critical condition 2 (X_{Vfc2} , W_{pc2}) were tested: Method 1 (Lower viscosity in the particles). Critical point of $X_{Vfc2} = 0.84$ ($W_{pc2} = 0.7945$) in interval III of polymerization (zero monomer droplets); Method 2 (Middle viscosity in the particle). Critical point at $X_{Vfc2} = 0.84$ ($W_{pc2} = 0.7945$) and $V_{fc2} = 0.05$. This critical point is present at a higher conversion than that at the beginning of interval III, and Method 3 (Higher viscosity), without these critical points, therefore there is not increment of $k_{p,BuA}$. Thus, Method 2 is a bridge between Method 1 (earlier increment of *BuA* k_p) and Method 3 (not increment of *BuA* k_p value). On this way, we have found that a lower viscosity in the particles produced an earlier increment of *BuA* k_p value (for whichever batch, Method 1) and that a higher viscosity in the particles did not produce an increment of *BuA* k_p value (SC-1, SC-3 and BS-1, Method 3). Methods 1 and 2 were almost equivalent in the batch processes because the critical condition of Method 2 was obtained in interval III of polymerization as Method 1 (near $X_0 = 80$ wt%).

The values for almost all the parameters for this model of the terpolymerization of *St/MMA/BuA* were found in the literature. We consider that the selection of these parameters was adequate because the selection was based on similar conditions to the experimental ones. When there were several different values for a parameter one of them close to the average of them was taken for our simulations. On this way, they were selected not with the intention of obtaining the best fitting of the kinetic outputs, but by using a chemical and physical criterion of similar conditions to those of the experimental runs [12].

In order to fit the conversion, we have realized that there are four remaining unknown variables: The saturation concentration of monomers in the particle $[M_i]_{p,sat}$, the ratio of the water mass transfer side resistance to overall mass transfer for desorbed radical " δ_i ", the three k_{p-gel} models and the three methods for evaluating the effect of viscosity on the k_{p-gel} effect. With this in mind, we have used the values of $[M_i]_{p,sat}$ found in the previous work: $[M_{St}]_{p,sat} = 5.6$, $[M_{MMA}]_{p,sat} = 4.4$, $[M_{BuA}]_{p,sat} = 4.5$ (mol/dm³) for intervals I and II with the hypothesis that a higher concentration of *St* in the particle decreases the solubility of *MMA* in the particle. We have used the Maxwell rule for calculate the instantaneous monomer concentration in the particle $[M_i]_p$ in intervals I and II [12]:

$$[M_i]_p = \sum f_{ip} [M_i]_{p,sat} \quad (14)$$

Where f_{ip} is the fraction mol of monomer *i* in the particle in relation to all monomers. We have found that for B-1, the monomer *MMA* was more solubilized in the

particle than the other monomers, that is, $[MMA]_p$ was higher [12]. On this way, the saturation lower concentration of *MMA*, $[M_{MMA}]_{p,sat} = 4.5$ mol/dm³, did not avoid of having a higher solubilization of *MMA* in the particle than the other monomers, but the maximal solubilization decreased but the presence of the other monomers. In the case of interval III, we have used the saturation values reported in the literature: $[M_{St}]_{p,sat} = 5.6$, $[M_{MMA}]_{p,sat} = 6.9$, $[M_{BuA}]_{p,sat} = 5.2$ (mol/dm³) and the prediction was accurate, as for example observed in the semicontinuous processes [12]. On the other hand, we have varied the other three parameters: δ_i in the range [0.02, 0.16], the k_{p-gel} models (Ray, W_p , Hamielec) and the three methods for taking into account the viscosity on the k_{p-gel} effect. The range of δ_i between [0.02, 0.16] was used by Ginsburger [46], and also by Nomura and Fujita [24] for *St*, *MMA* or *BuA* [12]. For simplicity, we have given the same value of δ_i for all the monomer radicals, so $\delta = \delta_i$ as Nomura and Fujita have found for *St* and *MMA* [24]. The values of the constants of the k_{p-gel} effect for all the processes were found by adjusting the conversion of batch B-1, taken as a reference, as explained above and in the previous work [12]. From these k_{p-gel} models and the three methods which take into account the effect of the viscosity, the most adequate model was selected by considering the lowest error in the fitting to the experimental data. After that, we have verified the that the $[M_i]_{p,sat}$ the constants of the $k_{p,gel}$ effect for the Hamielec's model and the critical free volume V_{fcc} were optimal through the optimization of the values by the algorithm evolutive reported by Kukkonen [47,48] with the aid of a previously found optimum by trial and error. In fact, the optimal $k_{p,gel}$ effect constants for the Hamielec's model have a physical meaning as explained above. It is important to mention that the sensitivity of the models to the above mentioned parameters was very low and then a change of the mean square error MSE of 0.1 wt% for X_0 [12] can be considered important. In the selection of the best models for the semicontinuous processes, we also considered an MSE of the accumulated conversion $X_{ac} < 0.5$ wt% and the best fitting to the conversion at the end of the addition of the monomers, as occurred with semicontinuous SC-3. Two examples of the manner for selecting the best k_{p-gel} models are given in Supporting Information Section S-3. On the other hand, the condition of k_{p-gel} effect in the radical desorption rate R_i was critical in batch B-3 in order to adjust the molecular weights. This condition was used for the other processes in which the k_{p-gel} effect in R_i was not critical for the evaluation of the molecular weights, as explained in Supporting Information Section S-1.1. All the processes were simulated with k_{p-gel} effect in the kinetic rate of polymer radical transfer to monomer, condition which was critical for the seeded BS-1. Besides, as a chemical congruence the k_{p-gel} effect was present in

the propagation rate of the tertiary radicals and transfer to chain transfer agent for all the radicals.

In the literature there are reported works in which the outputs conversion, molecular weight, diameter of particle [46] are considered simultaneously in the parameter estimation algorithm in order to find their optimum values that give the best fitting of the experimental data with the simulation results. In the present work we have chosen a different approach, a sequential one, in which the conversion is fitted first [12] because a valid value of molecular weight needs a correct value of conversion and there is more accuracy in the determination of conversion output than in the other two outputs.

VI. RESULTS

All emulsion terpolymerization processes were simulated taking into account: 1. The decrement of the value of k_p by the k_p -gel effect, 2. The possibility of increment of the k_p value of BuA by the higher proportion of BuA in the terpolymer, as above has been explained. All the better k_p -gel models gave acceptable approximations to the experimental conversion curves, however, always was one that gave a slightly better fitting and then it was chosen as the best k_p -gel model as shown in Fig. 2. The best fitting to the experimental data by the simulation curves obtained with the Hamielec's, Ray's and W_p models were the following (here we are reporting all the cases which satisfied the MSE uncertainty): B-1 (Method 1, best: W_p , second best: Ray, $\delta = 0.02$), B-2 (Method 1, Hamielec, $\delta = 0.02$), B-3 (Method 1, best: Ray, second best: W_p , $\delta = 0.02$), B-4 (Method 1, Hamielec, $\delta = 0.02$), SC-1 (Method 3, best: Ray, second best: W_p , $\delta = 0.04$, second best: 0.05), SC-2 (best: Method 2, second best: Method 1, W_p , $\delta = 0.02$), SC-3 (Method 1, best: Hamielec, best: $\delta = 0.04$; second best: Ray, second best: $\delta = 0.02$), SC-4 (Method 3, Hamielec, $\delta = 0.02$), BS-1 (Method 3, W_p , $\delta = 0.16$). We must emphasize that the selection of the method (1, 2 or 3) was dependent on the value of the polymeric solution viscosity inside the particles at the critical point when the proportion of BuA is higher than $X_{vic,BuA}$: for processes with a low viscosity then Method 1 should be employed, for high viscosity then Method 3, for a middle viscosity then Method 2. All the batch processes were simulated by Method 1 because their low viscosity at the critical point. Besides, the most similar semicontinuous process to the batch B-1, to say, SC-3, was also simulated by Method 1. The semicontinuous SC-3 had the higher addition rate of monomers and then a lower viscosity in the particles than the other semicontinuous. On this way, it was expected that the polymer particles formed in SC-3 were more similar to the batch process B-1. On the opposite the semicontinuous processes with lower addition rate of monomers, SC-1 and SC-4, had more

constraints to the diffusion. This was consequence of the higher proportion of the polymer. The higher proportion of polymer produced a higher viscosity in the particles and then Method 3 (the higher viscosity in the particle does not allow the increment of $k_{p,BuA}$) was more suitable for fitting the conversion. Then, these processes did not have a critical point for an increment of the BuA propagation coefficient. In the same trend, the seeded semicontinuous process BS-1 was simulated by Method 3 due to have the highest proportion of the polymer and then a higher viscosity.

As observed in the previous work [12]; A). The k_p -gel effect in the batch processes is stronger in the W_p and Ray's models and lesser in the Hamielec's model (See Fig. S2, Supporting Information). On this way, the simulation of the semicontinuous process BS-1 by the W_p k_p -gel model indicates the k_p -gel effect is stronger in this process, B). The increment of the addition of monomers decreases the effect of the k_p -gel effect (SC-1 with the lowest addition rate simulated by Ray's and W_p models and SC-3 with the highest addition rate simulated by Hamielec's model), C). A higher rate of polymerization R_p (due to a higher temperature in B-4) produces that the k_p -gel effect is lower in this batch process and then the process is simulated by the Hamielec's k_p -gel model. The same increment of R_p was found by the higher amount of emulsificant in batch B-2 and then the Hamielec's k_p -gel model best fitted this process. On this way, we can say that an increment in the rate of polymerization R_p with respect to B-1 make the batch more prone to be simulated by Hamielec's k_p -gel model.

On the other hand, at exception of BS-1 with $\delta = 0.16$, all the batch and semicontinuous processes have a δ near to 0.02, indicating that the radical desorption was not appreciable. All the batches have the minimum desorption with a value of $\delta = 0.02$ and the highest desorption of the semicontinuous was in SC-1 and SC-3 with $\delta = 0.04$. The value of δ for the semicontinuous process SC-2 and the batch process B-1 was 0.02, SC-3 as intermediate process between SC-2 and the batch process B-1 should also have a value of $\delta = 0.02$, but it has a value of 0.04. This higher value of δ in SC-3 probably indicates that the higher addition rate of monomers produced a lower proportionality between the polymerization and desorption rates R_p/R_t because the desorption of the monomeric radicals was higher.

On the other hand, it was observed that in all the processes the coefficient of desorption $K_{f,BuA}$ was the highest one, Vg., $K_{f,St} = 0.0384$ 1/s, $K_{f,MMA} = 0.544$ 1/s, $K_{f,BuA} = 0.792$ 1/s in B-3; $K_{f,St} = 0.164$ 1/s, $K_{f,MMA} = 2.24$ 1/s, $K_{f,BuA} = 3.37$ 1/s in SC-4 (see equations in Table S1, Supporting Information as a reference). Then, the value of $\delta = 0.02$ in SC-4, where the amount of BuA was higher in the feed, indicates that the resistance to

desorption of the BuA monomeric radicals in SC-4 was similar to the batch processes. It was also found that the radical desorption was the highest ($\delta = 0.16$) in the seeded semicontinuous process with higher diameter of particle, BS-1, indicating that the resistance to water diffusion outside the particles fell down dramatically in relation to the batch processes.

In Fig. 2 are given the fittings of the set of models which includes the backbiting for the BuA-ended radicals and for comparison are shown the fittings by the average k_p - k_t set of models of the previous work [12]. As observed, the batches B-1 and B-3 were best simulated by models which include the backbiting of BuA than the models which used the average values of k_p - k_t .

The batch process B-4 had a higher polymerization rate caused by a higher temperature of reaction than B-1. The best fitting was achieved by the average Hamielec k_p - k_t model than by the Hamielec's model which includes the backbiting of BuA. Indeed, the last model predicts a visible point of change of curvature of the rate of polymerization. We consider that, as a consequence of the high experimental polymerization rate R_p , the point of change of curvature is not appreciable in the data of B-4. Another possible explanation to this fact is that the dependence of the critical values XV_{fc} and/or V_{fc} on the molecular weight of the terpolymers could soften this change of curvature.

The fitting of the conversion curve for the semicontinuous processes was similar in the selected best models for both the k_p - k_t average and the BuA backbiting set of models, as seen in Fig. 3. The maximum difference was in the semicontinuous SC-1 and it was necessary to adjust the value of δ to 0.04 instead of 0.02 in the backbiting models for obtaining a best fit. The k_p - k_t average gel model for fitting SC-1 was the Benyahia's model which used $\delta = 0.16$ with $MSE_{x_0} = 1.25$ wt% and $MSE_{x_{ac}} = 5.06$ wt%. A higher value of δ could improve the accuracy of the fitting, but it is outside our valid range of δ [0.02, 0.16]. It was found that the fitting of the Benyahias' k_p - k_t average gel model with a fixed value of $\delta = 0.02$ which used Method 3 was poorer than the Ray's k_p backbiting gel model with $\delta = 0.04$ which used Method 3 with $MSE_{x_0} = 1.09$ wt% and $MSE_{x_{ac}} = 3.35$ wt% in the last model. This indicates that fitting of the k_p - k_t average Benyahia's k_p -gel model is less probable. On this way, the backbiting procedure gives more insights on the value of δ in emulsion terpolymerization.

In the semicontinuous processes it was found a similar trend in the selection of the k_p -gel model as in the batch processes: a higher polymerization rate R_p makes more suitable the process to be simulated by a free volume Hamielec's V_f k_p -gel model. On this way, the process SC-3, with the highest R_p , was simulated by the Hamielec's V_f k_p -gel model. On the other hand, the process SC-1, with the lowest polymerization rate R_p in

semicontinuous, was simulated by Ray's and W_p k_p -gel models.

We have found that the semicontinuous process SC-4 with a higher proportion of BuA than SC-1, had a lower k_p -gel effect and then it was simulated by the Hamielec's V_f k_p -gel model. We conjecture that in this semicontinuous process the higher free volume in the particle (caused by the higher proportion of BuA in the terpolymer and in the monomers) led to a lower k_p -gel effect. On the other hand, the process semicontinuous BS-1 was better simulated by W_p with Method 3, which indicates a higher influence of the viscosity on the increment of the k_p -gel effect. We hypothesize that the higher proportion of polymer in the particle caused this behavior.

We consider that the internal structure of the particle near its surface is different in the batch and semicontinuous processes. Under this hypothesis, the viscosity of the particles and consequently the importance of diffusion of the polymer radicals in the batch processes are lower than in the semicontinuous processes, as it is detailed below. Okubo et al. [49] also found a lower viscosity in a seeded PSt emulsion polymerization with a previously absorbed monomer of MMA (batch process) than in a semicontinuous process in which MMA was added. They also encountered that the surface morphology of the particles was similar at the end of the reaction for both methods. In the emulsion terpolymerization of St/MMA/BuA, the higher viscosity in the particles of the semicontinuous processes was corroborated by the experimental lower conversion after the end of the addition of the monomers. This fact was also encountered in the work of Urretabizkaia et al. [50]. The lower conversion at the end of addition of the monomers was more visible in the semicontinuous SC-1 and in the seeded process BS-1 as seen in Fig. 3. The higher viscosity at the end of the reaction also indicates that the internal structure of the particles in the batch processes is different to that in the semicontinuous processes. The difference of internal structure is at least in the number and size of the domains of the sequences riches of monomers of St and MMA in the terpolymer St/MMA/BuA. Okubo et al. [49] have pointed out this difference of internal structure for the case of PMMA or PSt domains in the mentioned emulsion homopolymerization of MMA in seeds of PSt.

In the same context, Sundberg et al. have demonstrated that acrylic polymers with a lower T_g allows a higher diffusion of the polymer radicals. On this way, it has been found a difference of three orders of magnitude in the diffusion coefficients in the case of styrene polymeric radicals in a seed of PMMA with a T_g of 387 K in comparison with a seed of polymethylacrylate PMA with a T_g of 289 K [18]. Consequently, it is expected that the friction ξ_{seg} in a terpolymer with a high proportion of BuA ($T_{g,PBuA} = 229$ K, [22] See Table S-3, Supporting Information) is much

lower than in the terpolymers with a higher proportion of St or MMA near the surface. For this reason, the diffusion of j-ended radicals is higher in BuA richer domains in the particle. On this way, it was expected a more uniform distribution of St and MMA in the particle in the semicontinuous processes SC-1, with no appreciable islands of BuA. SC-1 had the lowest addition rate of monomers, and consequently, the reaction took place near the surface which was enclosed by subsequent reaction steps. Due to the uniform distribution of MMA and St in SC-1, the viscosity was higher than in batch B-1, in which the distribution of MMA and St was more at random. This randomness was produced by the polymerization in the interior of the particles as a consequence of a higher concentration of monomers and higher diffusion of j-ended radicals inside the particle in B-1 than in SC-1. The higher viscosity was more perceptible after the end of addition of the monomers in SC-1. Consequently, the more uniform distribution of domains of St and MMA in the interior of the particle in this process decreased strongly the polymerization rate at the end of the addition of the monomers as also observed in BS-1 (Fig. 3). Indeed, this change of kinetic behavior at the end of the addition of monomers points out that the consumption of the monomers, after the end of their monomers addition, was from outside to inside the particle. It can be argued the for validating this hypothesis, the diameter of the batch and semicontinuous processes must be similar, but the problem is that the diameter of particles in semicontinuous are commonly lower as seen in Fig. 1 of the previous work for batch B-1 and SC-1 [12]. Nevertheless, we have found that a lower experimental conversion at the end of the reaction was found also in the seeded semicontinuous BS-1 with a higher particle diameter than the batch process B-1 as seen also in Fig. 1 of the previous work. This means that at the end of the addition of the monomers in the semicontinuous processes (with whichever particle diameter), at least the particle surface is different to that of the batch processes. This is reinforced when we analyze that the semicontinuous processes SC-2 with a higher addition rate of the monomers than SC-1 presented a higher experimental polymerization rate in relation to the simulation after the end of the addition of the monomers as seen in Fig. 3. For this reason, we have concluded that SC-2 had particles more similar in structure to the particles of the batch process B-1.

In relation to the outputs of conversion, composition of monomers in the terpolymer, molecular weight and DSC thermograms, they are very similar for both the k_p - k_t average set models and BuA backbiting set models. The conversion curves have already been analyzed, the similarity in the composition is analyzed in Supporting Information Section S-4. On the other hand, the desorption rate of monomeric radicals R_t in the backbiting set of models is more important than in the

k_p - k_t average set of models. This concept and the analysis of the molecular weight are given in Supporting Information Section S-5.

In relation to the DSC thermograms, in Table 9 are reported the experimental and simulated range of variation of T_g , $\Delta T_{g,DSC}$, of the batch and semicontinuous processes (See Supporting Information Section S-6. for the procedure and respective equations to simulate the DSC Thermograms). The value of the experimental ΔT_g is given by the intersection of the upper and lower extrapolations of the baseline at the onset of the inflexion [51]. In the case of the simulation, in order to define with more precision the onset for the beginning of T_g , we adjusted the initial baseline to be horizontal. Besides, in Table 9 is given the range of variation of the simulated instantaneous glass transition temperature ΔT_{gi} . Indeed, the lower value of ΔT_{gi} corresponds to the onset of the change of curvature of the simulated DSC Thermogram. It was also found that the simulation of the DSC thermograms was similar for the k_p - k_t average and backbiting including models.

The simulated $\Delta T_{g,DSC}$ for the batch processes has similar values of T_g and a wider range of ΔT_g that the experimental one as observed for B-1 in Fig. 4. This corroborates the results of the simulation. On the contrary, the simulated $T_{g,DSC}$ for the semicontinuous processes with a composition similar to B-1 (SC1, SC-2, SC-3) have higher values of T_g and a narrow range of $\Delta T_{g,DSC}$ that the experimental one. Besides, the final values of T_g were similar for the experimental and simulated semicontinuous processes. The discrepancy between the experimental and simulation results can be due to the fact that homogeneous nucleation was present in SC-1, SC-2 and SC-3 and then lower values of T_g were obtained. On the other hand, it is interesting to note that the simulation of ΔT_g of the semicontinuous SC-4 with a feed composition rich in BuA was correctly simulated by the $\Delta T_{g,DSC}$ program. This indicates that in the semicontinuous process SC-4 the homogenous nucleation was not important and that the range of micellar nucleation was given by $\Delta T_{g,DSC}$. In addition, $\Delta T_{g,DSC}$ for the semicontinuous process SC-2 (See above) was better simulated than that for the processes SC-1 and SC-3. For example, for SC-1: Experimental ΔT_g : 29-61 °C; Simulated ΔT_{gi} by backbiting model: 58-61 °C. SC-2: Experimental ΔT_g : 27-69 °C; Simulated ΔT_{gi} by backbiting model: 45-61 °C. In principle, SC-2 had an intermediate monomers addition rate between SC-1 and SC-3. These results indicate a higher homogeneous nucleation at lower and higher monomers addition rates, but not at intermediate monomers addition rate.

VII. DISCUSSION

a) Number of j-ended radicals

The rate of generation of tertiary radicals $R_{ncbb}(P_{ijk})$ was more important at the end of the reaction

for the batch B-3 and for the semicontinuous SC-4, as seen in Fig. 5. In consequence, the amount of tertiary radicals in the particle was appreciable at the end of the reaction, as seen in Fig. 6.

At all time, the number of tertiary radicals was mainly diminished by the propagation reaction $R_{p,ncbb}$. On the same way, the rate of propagation of the tertiary radicals $R_{p,ncbb}$ was higher in the process semicontinuous SC-4 than in the batch process B-3 at the beginning of the reaction (See the dashed line in Fig. 5 used as a reference). Then, there was more branching in SC-4 than in B-3 since the beginning of the reaction, as seen below in Fig. 12. So, the batch process B-3 did not present tertiary radicals until $X_0 = 65$ wt% as seen in Fig. 6 and in consequence B-3 had no branching. On the other hand, the increment of BuA-ended tertiary radicals n_{BuA} in SC-4 is caused by having these radicals a degree of polymerization greater than 3 because the backbiting needs a reaction of a BuA-secondary radicals with the antepenultimate BuA monomeric unit of the chain. Since the model considers only the monomeric radical desorption (degree of polymerization of 1) and also due to the low reactivity of the BuA-ended tertiary radicals, it is produced an accumulation of these radicals in the particle.

It noteworthy to clear up that the abrupt changes in the number of radicals in Fig. 5 is due to the

transition of interval II to interval III of emulsion polymerization ($X_0 \approx 40$ wt % in B-3), the presence of almost only tertiary radicals in the particle ($X_0 \approx 80$ wt % in B-3), the end of addition of monomers in semicontinuous ($X_0 \approx 80$ wt % in SC-4) and the beginning of the increment for k_p , BuA due to the gel effect. The abrupt change of the number of radicals can also be due to the increment of the $k_{p,BuA}$ due to the k_p gel effect, as it happens in SC-3 ($X_0 \approx 16$ %). These abrupt changes in the number of radicals or $k_{p,BuA}$ produced abrupt changes or shoulders in the values of conversion, diffusion, total k_p and instantaneous branching of the terpolymer, as seen in Figs. 2-11.

We have compared the number of j-ended radicals simulated to the number of j-ended radicals of the BuA-backbiting model with the k_p - k_t average model for the batch and the semicontinuous processes. We have found the kinetic variation of the radicals in both models is attenuated when we evaluate the ratio of the product of $k_{p,Tot} n_T$ between the BuA backbiting model and the k_p - k_t average model, R_{KpT} .

$$R_{KpT} = \frac{(k_{p,Tot} n_T) \text{BuA backbiting including model}}{(k_{p,Tot} n_T) Kp - Kt \text{ average model}} \quad (15a)$$

Where

$$R_p = \left(\sum_{i,j} (k_{p,ji} n_j [M]_{i,p}) N_p \right) = k_{p,Tot} n_T [M_T]_p N_p \quad i = a, b, c; j = a, b, c, cbb. \quad (15b)$$

In Supporting Information Section S-7 is given the example for batch B-3.

b) Gel effect

The increment of BuA k_p was analyzed through the behavior of the free volume V_f , the fraction of free volume of BuA in the terpolymer X_{vfc} and the fraction of polymer W_p for SC-2 in Fig. 7 (The batch B-1 is analyzed in Supporting Information Section S-3.1).

In the case of the semicontinuous process SC-2, the limit of $X_{vfc2} = 0.84$ was exceeded since the beginning of the reaction ($X_0 = 11$ wt%) as seen in Fig. 7. If we included the limit of $X_{vfc2} = 0.84$ for the increment of the k_p of BuA as occurred for the Ray and Hamielec k_p free volume gel models with Method 1, the conversion would be higher. On the opposite, the limit $W_p = 0.7945$ in the semicontinuous process SC-2 was gotten at almost the end of the addition of the monomers and then W_p model with Method 1 fitted better the conversion experimental curve than Ray and Hamielec k_p free volume gel models with Method 1. On the other hand, Methods 1 and 2 gave similar results because the critical value $W_p = 0.7945$ was the value

that was relevant and gotten at the end of the reaction, but Method 2 was slightly better. For this reason, Method 2 was the one selected.

In order to find a microscopic explanation for the fact that R_p indicated what k_p -gel model was used to simulate the conversion curve, we have encountered that the batch B-4 had more radicals per mol of monomer $\#R/n$ (Equation (5c)) than the batch B-1, as seen in Fig. 8. We have considered that the time required by a monomer to approach one radical was lesser in B-4 with a higher amount of radicals than in B-1. Also the j-ended polymer radicals had to make shorter movements for reacting with the monomers. Thus, a higher number of radicals per mol of monomer $\#R/n$ caused a minor movement by diffusion of the radicals (segmental or translational) in order to react with a monomer. We have expressed the rate of polymerization R_p in function of $\#R/n$ in order to clarify the weight of $\#R/n$ in the selection of the k_p -gel model as seen in Equation (16a)-(16b).

$$R_p = k_{p,Tot} n_T [M_T]_p \frac{N_p}{N_A^2} = k_{p,Tot} n_T [M_T]_p \frac{V_p}{v_p N_A^2} \quad (16a)$$

$$R_p = k_{p,Tot} \frac{n_T}{[M_T]_p} \frac{1000}{v_p} \frac{[M_T]_p^2 V_p}{1000 N_A^2} = k_{p,Tot} \frac{\#R}{n} \frac{[M_T]_p^2 V_p}{1000 N_A^2} \quad (16b)$$

Where V_p is the total volume of the particles ($\text{cm}^3_p/\text{cm}^3_w$), v_p is the volume of one particle ($\text{cm}^3_p/\text{part}$). On this way, a higher value of R_p is obtained by both increments of $k_{p,Tot}$ and $\#R/n$. We can say that there is a synergistic effect of the increment of $k_{p,Tot}$ and $\#R/n$ (through R_p) to decrease the k_p -gel effect. This leads to select the Hamielec's free volume model (Ham) for fitting the conversion curve, as happened for B-2, B-4 and SC-3, all with the same feed composition and with the higher values of $\#R/n$ as seen in Fig. 8. On the other hand, the processes B-1 and SC-2 were simulated by the W_p k_p -gel best model (W_p) and the process SC-1 by the Ray's best free volume model (Ray) and then have lowers values of $\#R/n$ as seen in Fig. 8. The same behavior was found for processes B-3 and SC-4 which have both the same feed composition: SC-4 was simulated by the Hamielec's k_p -gel effect model by having a higher value of $\#R/n$ than B-3 (Ray's k_p -gel effect model) as also seen in Fig. 8. On the other hand, it is also observed in Fig. 8 that the process semicontinuous SC-3 has an abrupt change of slope in the variation of $\#R/n$ vs conversion curve. This abrupt change was consequence of the higher polymerization rate R_p at $X_0 = 18$ wt% because the critical point X_{vic2} for the increment of k_p of BuA was achieved. Then, the constant of the k_p -gel effect changed from 0.350 to 0.108 in the Hamielec's V_f k_p -gel effect model (See Table 3).

c) Diffusion coefficients and its relation to the k_p -gel constants

Having validated the results of the model, we have calculated the diffusion coefficients in the emulsion terpolymerization of *St/MMA/BuA*. We have found that the k_p - k_t average set of models had more uncertainty in the values of k_p^{diff} in accordance to Equation (4). This was consequence of the lower variation of the total propagation coefficient $k_{p,Tot}$ in this set of models in relation to the total propagation coefficient without gel effect $k_{p,Tot0}$. For this reason, there were zones in which the values of k_p^{diff} were negative, which does not have a chemical meaning. On the opposite side, the diffusion coefficients obtained in the BuA backbiting set of models have always positive values, by this reason we have only used the values of this set of models. This is the reason why the models using backbiting are useful for the evaluation of diffusion coefficients in the terpolymerization of *S/MMA/BuA*.

In Fig. 9 are shown the diffusion coefficient for the monomer D^M , the total diffusion coefficient for the contribution of monomers and polymer radicals D^{diff} , the diffusion coefficient of the polymer radical associated to

the termination and propagation $D^{PR,t}$, the diffusion coefficient of the polymer radical D^{PR} , the diffusion coefficient of the dead polymer D^P and the diffusion coefficient by reaction diffusion D^{rd} . In this figure it is observed that the diffusion of monomer D^M is several orders of magnitude higher than $D^{PR,t}$ and D^{PR} . The value of D^M corresponds to the diffusion of the monomers which falls down exponentially near the polymer as seen in the Fig. 8 of von Meerwall et al. for PSt [28]. In Fig. 9 is shown that the diffusion of monomers D^M at the beginning of the reaction was higher in the process B-1 than in the processes SC-1 and SC-3 in the sequence: B-1 > SC-3 > SC-1 (Vg. at $X_0 = 50$ wt%: $D^M = 14.5 \times 10^{-6} \text{ cm}^2/\text{s}$ for B-1 at $W_p = 0.52$ > $D^M = 5.3 \times 10^{-6} \text{ cm}^2/\text{s}$ for SC-3 at $W_p = 0.80$ > $D^M = 3.80 \times 10^{-6} \text{ cm}^2/\text{s}$ for SC-1 at $W_p = 0.80$). This sequence is related to the increment in the viscosity from B-1 to SC-1 and then to the lower rate of polymerization in SC-1. It is worth to mention that the value of D^M of these processes with BuA as third component is near to the experimental values of $D^M = 10 \times 10^{-6} \text{ cm}^2/\text{s}$ for MMA in PMMA at $W_p = 0.50$, and $D^M = 1 \times 10^{-6} \text{ cm}^2/\text{s}$ for St in PSt at $W_p = 0.50$ [13-14,18]. As it was observed for B-1 and SC-1, the terpolymer composition of BuA was near to 15 mol% at $X_0 = 50$ wt% (Supporting Information Section S-4) and this increased the diffusion of the monomers, as explained above. Indeed, the DSC thermograms indicate a higher T_g of the terpolymer at the beginning of the reaction and a subsequent decrement with the conversion (Supporting Information Fig. S1). On the other hand, the way to evaluate the diffusion coefficient of the polymer radicals and polymers was explained above. The similitude to the experimental values of the polymer diffusion coefficients D^P can be verified with the values of $D^P = 7.32 \times 10^{-9} \text{ cm}^2/\text{s}$, $M_w = 80,000 \text{ g/mol}$, *St/MMA/BuA* = 35/51/14 mol% and $W_p = 0.53$ at $X_0 = 50$ wt% for B-1 in relation to PMMA $D^P \approx 1 \times 10^{-8} \text{ cm}^2/\text{s}$ with $M_w = 90,000 \text{ g/mol}$, MMA = 100 mol% and $W_p = 0.50$ with the values of Faldi and Mills [13,45].

We consider then that the diffusion of the polymer radicals D^{PR} controls the details of the k_p -gel effect, in this case the selection between the V_f or W_p model. In order to verify this hypothesis, we have evaluated the effect of the diffusion coefficient D^{PR} in the selection of the k_p -gel model. We have weighted its influence by the product of n_T times D^{PR} ($\text{cm}^2/\text{s}/\text{particle}$), because a higher number of radicals increases the possibility of reaction with the monomers and then the k_p -gel effect is decreased. On this way, when we have analyzed the batch processes B-1, B-2 and B-4. The sequence of values of $n_T D^{PR}$ is B-1 < B-2 < B-4 (Vg. at $X_0 = 50$ %: $n_T D^{PR} = 16 \times 10^{-11} \text{ cm}^2/\text{s}/\text{part}$ for B-1 < n_T

$D^{PR} = 79 \times 10^{-11} \text{ cm}^2/\text{s}$ for B-2 < $n_T D^{PR} = 193 \times 10^{-11} \text{ cm}^2/\text{s}$ for B-4). This sequence is also shown in Fig. 10 and this progression is correlated to the change of using the Ray's k_p -gel model in B-1 to the Hamielec's k_p -gel model in B-4: A lesser global diffusion of the polymer radicals indicated by the product of $n_T D^{PR}$ implies that the friction is more important in the diffusivity of the polymer radicals. On this way, the selection of the k_p -gel model in SC-1 (Ray's V_f k_p -gel model) and SC-3 (Hamielec's V_f k_p -gel model) was also correlated to the values of $n_T D^{PR}$ (Vg. at $X_0 = 50\%$: $n_T D^{PR} = 0.16 \times 10^{-11} \text{ cm}^2/\text{s}$ for SC-1 < $n_T D^{PR} = 0.66 \times 10^{-11} \text{ cm}^2/\text{s}$ for SC-3). As observed, in Fig. 10, the selection of the k_p -gel model by this methodology is more limited than the selection based on the number of radicals per mol of monomer $\#R/n$ applied in Fig. 8 because we need to differentiate the batch and the semicontinuous processes. This is consequence of the lower values of n_T and D^{PR} in the semicontinuous processes.

In the batch B-1 is also observed that the diffusion of the polymer radical D^{PR} was lower than the diffusion of the (dead) polymer D^P (Vg. $D^{PR} = 153 \times 10^{-11} \text{ cm}^2/\text{s}$, $D^P = 732 \times 10^{-11} \text{ cm}^2/\text{s}$ at $X_0 = 50 \text{ wt}\%$) because the degree of polymerization was lower in the dead polymer ($N^{PR} = 652$, $N^P = 242$ for B-1) and the exponent in Equation (9) for obtaining D^{PR} and D^P is higher than 1. This was not the case for the semicontinuous processes in which the degrees of polymerization of the polymer radicals and dead polymers were similar (SC-1: $N^{PR} = 312$, $N^P = 321$). On the other hand, as a consequence of the low amount of j-ended radicals in the particle (in general, $n_T < 0.5$), the reaction diffusion D^{rd} was negligible in emulsion terpolymerization of *St/MMA/BuA*, as seen in Fig. 9.

When we compare the diffusion of the polymer radicals associated to termination $D^{PR,t}$ with the diffusion of the polymer radicals D^{PR} obtained by the method of moments of the molecular weight in the batch processes, it is observed a similar order of magnitude. This indicates that in the batch processes the termination is produced by the long radical polymer chains. On the other side, in the semicontinuous processes the diffusion of the polymer radicals associated to termination $D^{PR,t}$ is higher than the diffusion of the total polymer radicals D^{PR} . This is due to the lower degree of polymerization $N^{PR,t}$ of the short radicals associated to termination than the degree of polymerization of the total radicals N^{PR} which was obtained by the method of moments as discussed above. This corroborates the hypothesis that the short radicals have more influence in the termination rate [41,45]. On the other hand, the diffusion of the polymer radicals obtained by the method of moments D^{PR} for the batch B-1 (with a higher proportion of styrene, an aromatic monomer) was lower than those of the batch B-3 (with a higher proportion of aliphatic acrylic

monomers) (Vg. at $X_0 = 50 \text{ wt}\%$; $D^{PR} = 153 \times 10^{-11} \text{ cm}^2/\text{s}$ in B-1; $D^{PR} = 653 \times 10^{-11} \text{ cm}^2/\text{s}$ in B-3) as is also affirmed by Griffiths et al. [19] for aliphatic radicals. However, the diffusion coefficients of the polymer radicals associated to the termination reaction $D^{PR,t}$ are similar to ($D^{PR,t} = 438 \times 10^{-11} \text{ cm}^2/\text{s}$ in B-1; $D^{PR,t} = 416 \times 10^{-11} \text{ cm}^2/\text{s}$ in B-3 at $X_0 = 50 \text{ wt}\%$).

In Fig. 11 are shown the total propagation rate coefficient without gel effect $k_{p,Tot0}$, the total propagation rate coefficient with gel effect $k_{p,Tot}$, the propagation rate coefficient for the monomer k_p^M , the propagation rate coefficient of the total diffusion contribution of monomers and polymer radicals k_p^{diff} , and the propagation rate coefficient for the reaction diffusion k_p^{rd} for the batch process B-1, and the semicontinuous SC-3 and SC-1. The k_p -gel effect was higher in the process SC-1 and for this reason $k_{p,Tot}$ was almost one order of magnitude lesser than $k_{p,Tot0}$ (Fig. 11) As a consequence, the ratio $k_p^{diff}/k_{p,Tot0}$ for SC-1 was lower than the corresponding ones of batch B-1 and semicontinuous SC-3 (see Equation (4)). In other words, the diffusion of monomers was more important in SC-1 than in B-1 or in SC-3.

In Fig. 11 is also observed that the k_t -gel effect was stronger than the k_p -gel effect. In particular, the ratio of $k_t^{diff}/k_{t,Tot0}$ at the beginning of batch B-1 was higher than those of the semicontinuous processes SC-1 and SC-3 (Fig. 11), indicating a lower influence of the polymer radical diffusion on the batch B-1 termination rate.

d) Branching in the terpolymerization of *St/MMA/BuA*

We have calculated the averages of branching density BD and branching fraction BF. As seen in Fig. 12, the branching was not present in the batch process B-3, with a higher proportion of *BuA*, since the beginning of the reaction until $X_0 < 65 \text{ wt}\%$. On the opposite side, the processes BS-1 and SC-4, in which the monomers were added in semicontinuous, presented branching in the terpolymer since the beginning of the addition of the monomers. Nevertheless, these processes at the end of the reaction had a lower proportion of branching than B-3 ($BD = 18 \times 10^{-4}$ in B-3 > $BD = 12 \times 10^{-4}$ in BS-1 > $BD = 10 \times 10^{-4}$ in SC-4 at $X_0 = 96 \text{ wt}\%$). Then, the kinetic behavior of $R_{p,cb}/R_p$ (Equation (12a)-(12c)) in the reaction determines the accumulated branching at the end of the reaction. The seeded process BS-1 had a lower proportion of *BuA* and a lower amount of the chain transfer agent *n*-DDM than SC-4. The first condition caused that the branching fell down and the second that the branching went up (see Introduction section). The final result was that the branching density BD in BS-1 was higher than the branching of the semicontinuous SC-4. Besides, the values of BD are consistently one order lower than the experimental value of BD for a homopolymer of *BuA* without transfer agent ($BD = 131$

$\times 10^{-4}$ at 60°C) and of the same order when is used a chain transfer agent (BD experimental = 28×10^{-4} with CBr_4 at 60°C) [3]. On the other hand, the branch fraction BF is not a factor which determines the degree of branching BD. On this way, the seeded process BS-1 had the highest BF at $X_0 = 96 \text{ wt\%}$ (Vg. at $X_0 = 96 \text{ wt\%}$: BF = 30×10^{-4} in B-3, BF = 46×10^{-4} in BS-1 and BF = 19×10^{-4} in SC-4), but the branching of BS-1 was not as important as in B-3. As observed in Fig. 12, a higher addition rate of monomers B-3 > SC-4 produces a higher branching.

In principle, the rate of propagation of the tertiary BuA-ended radicals $R_{p,\text{cbb}}$ depends on the number of these radicals in the particle $n_{\text{c,bb}}$ (Table 1 and Figs. 5 and 6). We have not considered the length dependency of the propagation coefficient nor a lesser backbiting by a lesser degree of polymerization (2nd and 3rd hypothesis, respectively, see above), but have obtained a degree of branching similar to the experimental results. Then, it could be possible that only the abstraction of the hydrogen of the transfer agent *n*-DDM by the tertiary electrophilic radical was the ground for the decrement of the branching (1st hypothesis, see above).

We have also compared the branching in the processes B-1, SC-3 and SC-1 (with a sequence to lower addition rate and consequently lesser amount of monomers in the particle from left to right in Fig. 13). It was found a maximum of the branching density BD and fraction branching FB at $X_0 = 96 \text{ wt\%}$ in the semicontinuous process SC-3 with the intermediate addition rate of the monomers (BD = 14×10^{-4}) and a minimum degree of branching in B-1 (BD = 5×10^{-4}). On the other hand, the middle degree of branching was found in SC-1 (BD = 10×10^{-4}) but at a conversion higher than 96 % the higher branching was in the order B-1 > SC-3 > SC-1 (sequence of less rate of addition of monomers), see Fig. 13. We consider that not only the depletion of the monomers in the particle is an important factor for branching, but also the ratio $R_{p,\text{cbb}}/R_p$, at what conversion the branching begins and until what conversion are allowed to react with the monomers.

VIII. CONCLUSION

From the k_p - k_t average model for the emulsion terpolymerization of *St/MMA/BuA* previously developed, the inclusion of the reaction of BuA backbiting with the associated k_p -gel effect in the model allows to know in more exact detail the kinetic phenomena of the emulsion terpolymerization of this system. Indeed, the k_p - k_t average model is used as a guide in order to improve the results of the model which includes the BuA backbiting reaction with the associated k_p -gel effect. On this way, it is realized that the rate of desorption of monomeric radicals has influence on the molecular

weight and branching of the terpolymer of *St/MMA/BuA*. In a synergistic way, the results of both set of models support the hypothesis that the internal chemical structure of the particles grown in semicontinuous processes are different that the internal chemical structure of the particles produced in batch. This indicates that the distribution of sequences of monomers in the terpolymer throughout the particle in both kinds of processes was different. On the other hand, we have found that the gel effect depends on the ratio of the radicals to monomers and when this ratio goes up, the free volume model of Hamielec for the k_p -gel effect is more suitable for predicting the kinetic of the terpolymerization. When we have associated the gel effect to the diffusion of the monomers and polymer radicals, we have found that the diffusion of the total polymer radicals in the particle determines what k_p -gel model is adequate for simulating the gel effect. In this sense we can say that the k_p -gel model is a discrete one which takes into account these variables ($\#R/n$ or $n_T \cdot D^{\text{PR}}$) for the selection of the most convenient k_p -gel model. This selection was also dependent of the viscosity in the particle, and then we have used three methods in orders to give importance to the influence of the viscosity in the selection of the best method. Besides, the BuA backbiting including model allowed the evaluation of the average diffusion coefficients of the monomers, polymers and polymers radicals. On the other hand, based on the definition of branching density BD, ratio of rate of reaction of tertiary radicals to overall rate of polymerization for all the monomers, we have encountered that the evolution in time of the rate of addition of monomers modifies the percentage of branching.

a) Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Notation

- A_{jk} Constant " j " ($j = 1$ before; $j = 2$ after the critical point for BuA), for the k_p -gel effect of the different " k " models of the propagation rate coefficient k_p .
- b Bond length (cm).
- BD_i , BD Instantaneous branching density or average branching density.
- BF_i , BF Instantaneous branching fraction or average branching fraction.
- c^* Concentration for the overlap of the polymers in which they interpenetrate (g/cm^3).
- c^{**} Critical concentration of polymer for the onset of entanglements (g/cm^3).
- $C_{m,j}$ Monomer transfer constant for " j "-ended polymeric radical to monomer " j ".
- $C_{m,T}$ Chain transfer constant of i -ended radical to chain transfer agent T .

D_d, D_p Diameter of the droplet or particle (experimental and simulated) (cm, nm).

dn_{cbb}/dt Derive of the generation of BuA-ended tertiary electrophilic radicals (rad/part/s).

$D^d, D^M, D^{PR}, D^{PR,t}, D^p$ Diffusion coefficient, of the monomer near the polymer, of polymer radical or of polymer radical associated to the termination or of the dead polymer (cm^2/s).

$D^{d,}, D^{com,PR}, D^{com,PR,t}, D^p$ Diffusion coefficient induced by the reaction or the movement of the center of mass of the polymer radical or associated to the termination or the dead polymer (cm^2/s).

F_c Correction factor for the diffusion of the n-DDM from the droplets to the particles.

$f_{j,bb}$ Steric factor of the penultimate monomers "j" in the backbiting reaction of the BuA ended secondary radicals.

k_B Boltzman constant ($\text{g cm}^2/\text{s}^2/\text{K}$).

K_c Coefficient to calculate the beginning of critical concentration for the beginning of the entanglements (cm^3 (monomeric units) $^n/\text{g}$).

k_{cbb} Backbiting rate coefficient of the backbiting reaction of the BuA ended secondary radicals ($\text{dm}^3/\text{mol}_{\text{rad}}/\text{s}$).

$K_{r,j}, K_f$ Average desorption coefficient from the particle for monomeric radical "j" or for all the monomeric radicals ($1/\text{s}$).

k_p^{chem} Propagation coefficient dependent only on the reactivity of the monomers and j-ended radicals without considering the diffusion of the monomer and the polymer radical ($\text{dm}^3/\text{mol}_{\text{mon}}/\text{s}$).

k_p^{diff} Propagation coefficient dependent on the reaction diffusion of the monomer and the polymer radical ($\text{dm}^3/\text{mol}_{\text{mon}}/\text{s}$).

$k_p^M = k_p^{\text{rd},M}$ Propagation coefficient dependent on the reaction diffusion of the monomer ($\text{dm}^3/\text{mol}_{\text{mon}}/\text{s}$).

$k_{dr}^{\text{rd}} = k_p^{\text{rd},PR}$ Propagation coefficient dependent on the reaction diffusion of the polymer radical ($\text{dm}^3/\text{mol}_{\text{mon}}/\text{s}$).

$k_{p,\text{Tot}}, k_{p,\text{Tot}0}$ Overall propagation coefficient in the particle considering or not considering the gel effect ($\text{dm}^3/\text{mol}_{\text{mon}}/\text{s}$).

k_t^{chem} Termination coefficient dependent only on the reactivity of j-ended radicals without considering the diffusion of the polymer radical ($\text{dm}^3/\text{mol}_{\text{mon}}/\text{s}$).

k_t^{diff} Termination coefficient dependent on the reaction diffusion of the polymer radical ($\text{dm}^3/\text{mol}_{\text{mon}}/\text{s}$).

$k_{t,\text{Tot}}, k_{t,\text{Tot}0}$ Overall termination coefficient in the particle considering or not considering the gel effect ($\text{dm}^3/\text{mol}_{\text{mon}}/\text{s}$).

k_{tp} Overall termination coefficient in the particle considering the gel effect ($\text{dm}^3/\text{mol}_{\text{rad}}/\text{s}$).

$k_{v,jw}$ v = termination "t" ($k_{t,j}$ according to the german or USA convention $k'_{t,j}$) rate coefficient of i-ended radical to j-ended radical or polymerization "p" rate coefficient

of radical "i" to monomer "j" considering the gel effect at w = time "t" or without gel effect "0" ($\text{dm}^3/\text{mol}_{\text{rad}}/\text{s}$).

$L_{\text{pers}}, L_{\text{pers},i}$ Length of persistence of homopolymer "i" (cm).

$[M]_p, [M_T]_p$ Instantaneous monomer "j" or total monomer concentration in the particle "p" (mol/dm^3_p).

MSE Mean square error.

n_1, n_2 Exponents associated to the dependence of the diffusion coefficient to the degree of polymerization.

n_3, n_4 Exponents associated to the dependence of the diffusion coefficient to the concentration of polymer.

n, n_j, n_T, n_{ncbb} Average number of j-ended radicals without considering the tertiary electrophilic radicals or radical "j" in the particle or total average of radicals or ended tertiary radicals in the particle (rad/part).

$N, N^{**}, N^{PR}, N^{PR,t}, N^{PR,t}_{\text{max}}, N^{PR,t}_{\text{min}}, N^p$ Degree of polymerization in a the chain associated to the freely rotating segments or critical number of freely rotating segments which consider entanglements or degree of polymerization in a polymer radical in base to the moments of the molecular weight distribution or polymer radicals associated to the termination or maxima or minimum distribution of polymer radicals associated to termination in semicontinuous or degree of polymerization of a dead polymer.

N_A Avogadro's constant.

N_p Number of particles per unit volume of water ($\#/\text{cm}^3_w$).

$P_{ijk}(i,j,k)$ Probability of occurrence of the triad ijk with the j-ended radical "k".

$\langle r_0^2 \rangle^{1/2}$ Root mean square end to end distance of the homopolymer (cm).

$\#R/n = \#M/n$ Number of polymer radicals which react with the same number of monomers per mol of monomers (rad/mol).

R_f Desorption rate of all j-ended monomeric radicals (rad/part/s).

R_g Gyration radius (cm).

R_{kpnt} Ratio of the product of the $k_{p,\text{tot}}$ times n_T of the BuA backbiting including model between the same product for the k_p - k_t average model.

R_m Radical transfer rate to monomers of all j-ended radicals (rad/part/s).

R_{ncbb} Backbiting rate of the BuA-ended secondary radicals (rad/part/s).

R_T Chain transfer rate for all j-ended radicals to the chain transfer agent (rad/part/s).

R_p Total propagation rate of all j-ended radicals on mole basis ($\text{mol}/\text{cm}^3_w/\text{s}$).

R_p Propagation rate j-ended radicals (rad/part/s).

R_t Termination of the j-ended radicals (rad/part/s).

SBD, SBF Accumulated branching density or branching fraction at n iterations.

$V_f, V_{fcj}, V_{f,i0}$ Fraction of free volume in particle at time "t" or critical free volume before the critical point $j = 1$ or

after the critical point $j = 2$; or total free volume of the pure element l .

T, T_g Temperature, glass transition temperature or fusion temperature (K, °C).

$T_{g,i}, T_{gDSC}$ Instantaneous, accumulated and obtained by simulated by DSC glass transition temperature (°C).

$V_f^*, V_f^{Seg,*}$ Critical free volume for the beginning of the monomer or segment of the terpolymer to jump.

V_p Volume of one particle (cm^3_p).

V_p Total volume of the particles ($\text{cm}^3_p/\text{cm}^3_w$).

W_p, W_{pcj} Mass fraction of the terpolymer in the particle or critical mass fraction before the critical point $j = 1$ or after the critical point $j = 2$.

x Exponent associated to the micellar nucleation.

X_{ac} Accumulated mass conversion a time " t ".

X_o Monomers overall conversion (experimental or calculated).

X_{vf}, X_{vic} Proportion of *BuA* in the free volume of the terpolymer or critical value for the same parameter.

Greek Symbols

δ_j Ratio of the water mass transfer side resistance to overall mass transfer for desorbed radical " j ".

Δt Time step for the iteration of the program (s).

$\phi_{0,seg}, \phi_{0,i}$ Jump frequency of the polymer segments or monomer (1/s).

$\mu_0, \mu_1, \nu_1, \nu_2$ zero and first moments, of the living j -ended radicals; first and second moment of the dead polymers in the molecular weight distribution.

$\sigma_{LJ}^M, \sigma_{LJ}^R$ Diameter of Lennard Jones of the monomer or of the average of the j -ended radicals in the terpolymer (cm).

$\sigma_{SH}, \sigma_{SH,i}$ Hindrance factor or steric hindrance of monomer in terpolymer.

ΣR_r Sum of all the reactions of the *BuA* tertiary electrophilic radicals (rad/part/s).

τ Angle between bonds (°).

ξ_{seg} Friction coefficient of the segment of the polymer, in this case the monomer in the terpolymer (g/s).

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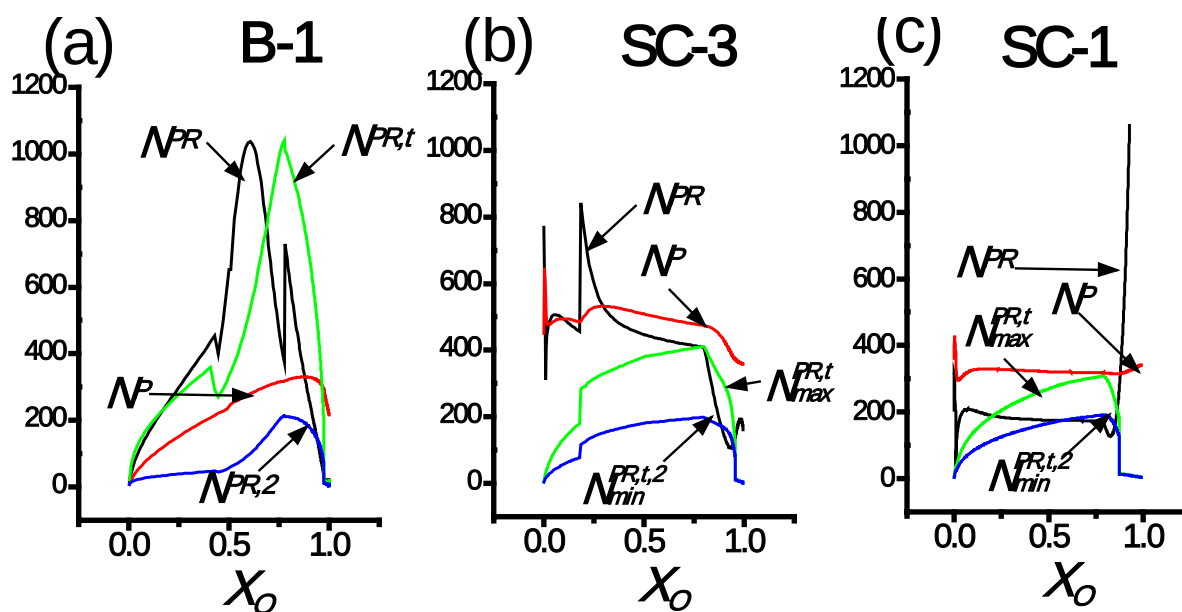


Fig. 1: Fitting of the values of degree of polymerization of the polymer radicals N^{PR} with the maximum degree of polymerization of the polymer radicals associated to the termination $N^{PR,t,max}$. N^P and $N^{PR,t,min}$ are also shown as reference (see text).

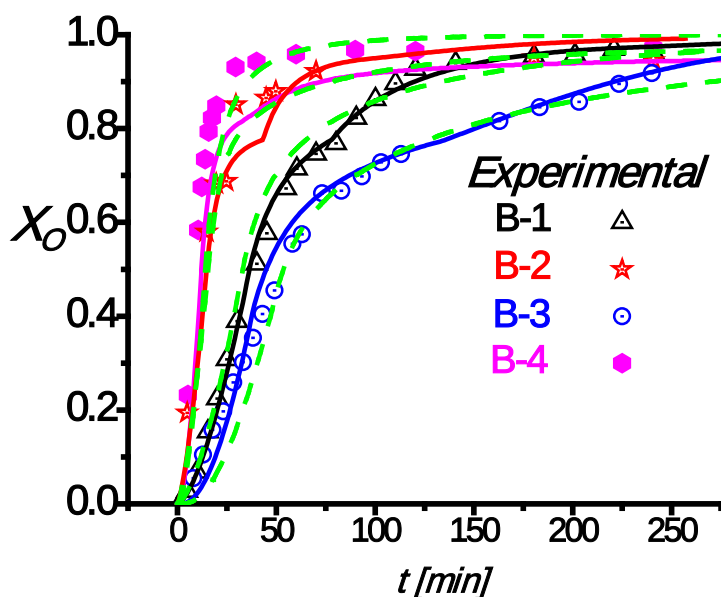


Fig. 2: Comparison of the simulation of the batch processes by the k_p - k_t average [12] (dashed lines) and the backbiting-including BuA set of models (solid lines), see text above.

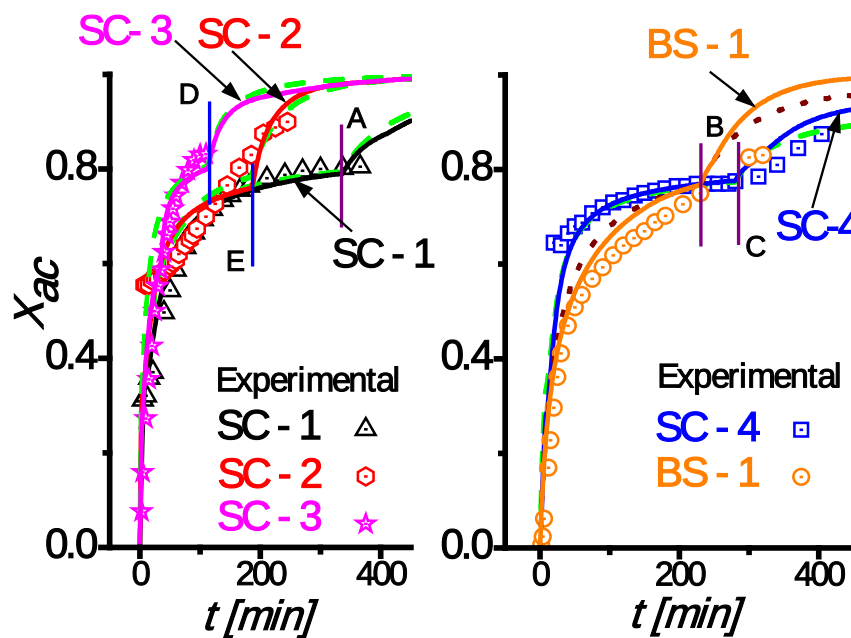


Fig. 3: Accumulated conversion X_{ac} for the semicontinuous processes SC-1 to SC-4, and for the seeded process BS-1 of the k_p - k_t average (dashed lines) and the backbiting-including BuA set of models (solid lines). The intersection of the lines A to E with the conversion curves of SC-1, BS-1, SC-4, SC-3, SC-2, respectively, indicates the conversion in which the addition of monomers has ended.

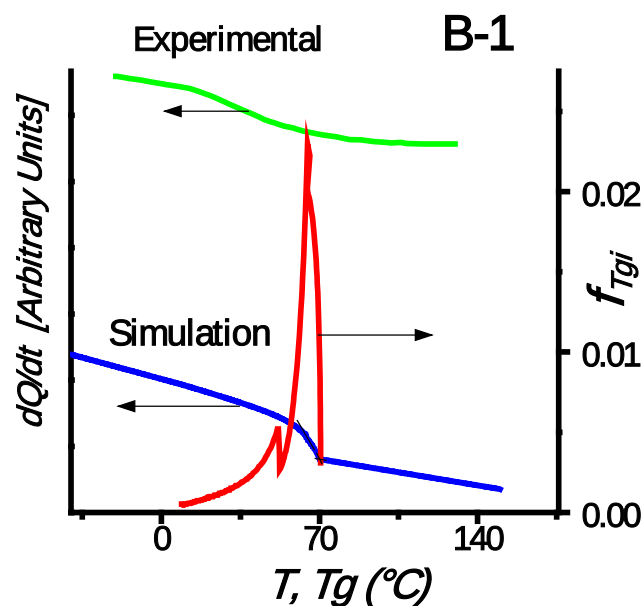


Fig. 4: Experimental and simulated curves by the backbiting model of DSC thermogram for B-1. The histogram of the instantaneous T_{gi} is also shown.

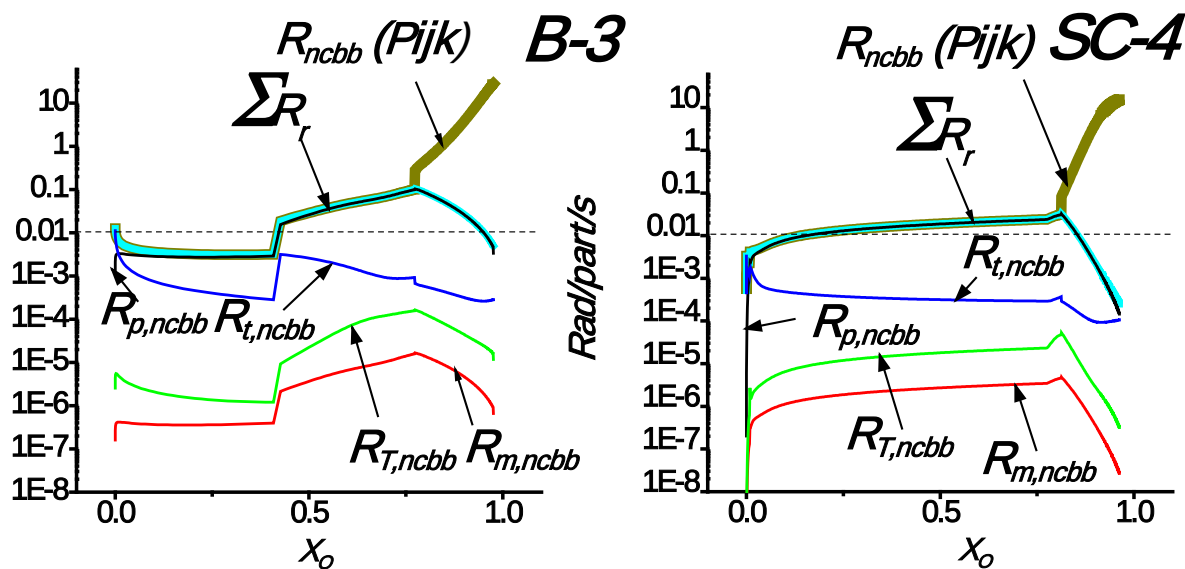


Fig. 5: Rates associated to the backbiting reaction (see text) in the processes batch B-3 and semicontinuous SC-4 with similar feed compositions.

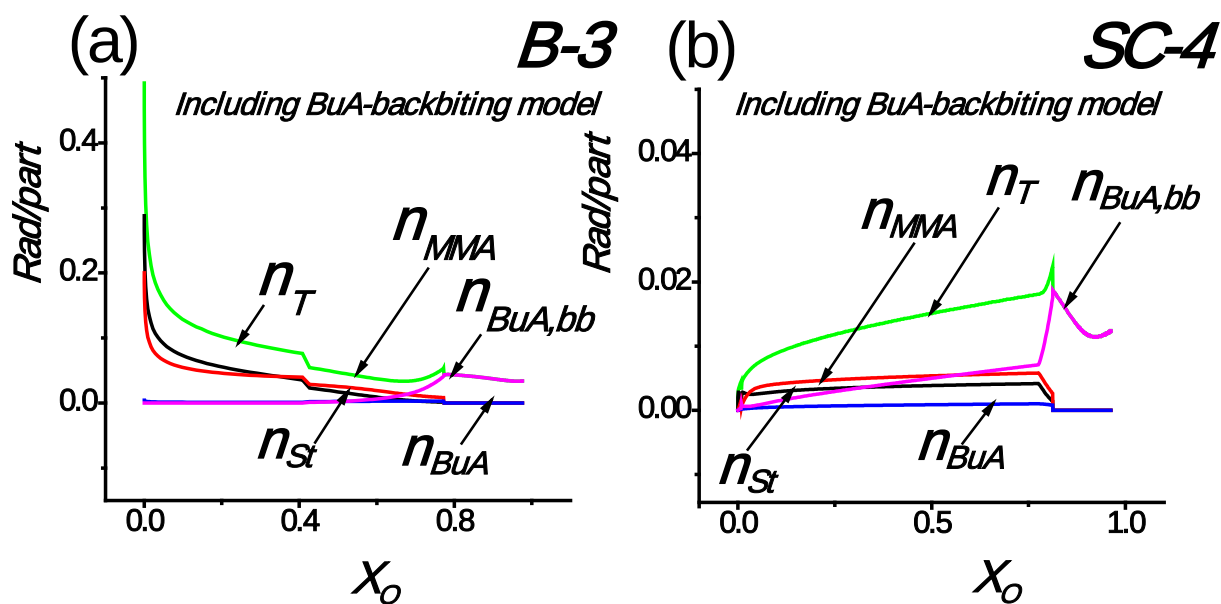


Fig. 6: Number of radicals for the batch B-3 and semicontinuous SC-4, which have the same composition in the including backbiting BuA model.

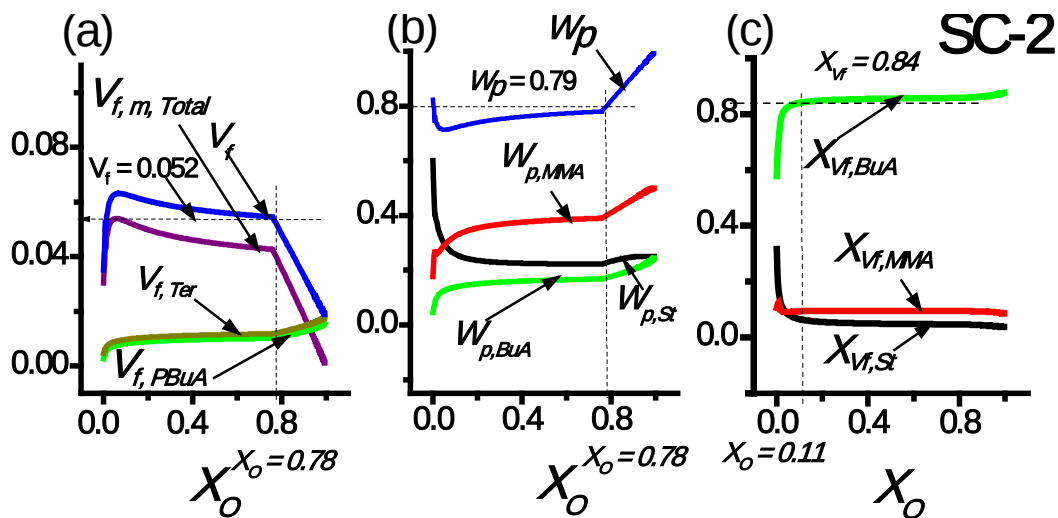


Fig. 7: Behavior of the (a). Free volume V_f , (b). Fraction of polymer W_p and (c). Fraction of BuA in the terpolymer X_{vf} for the semicontinuous process SC-2.

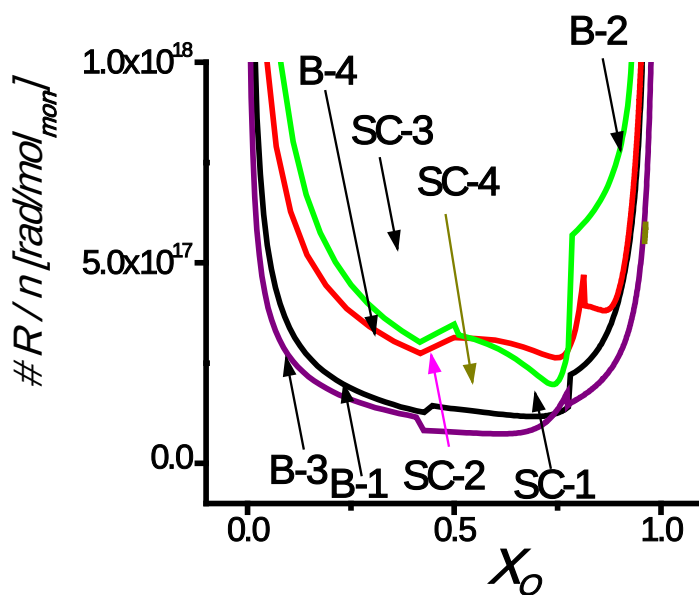


Fig. 8: Radicals per mole of monomer $\#R/n$ for the different process batch and semicontinuous of the terpolymerization of *St/MMA/BuA*.

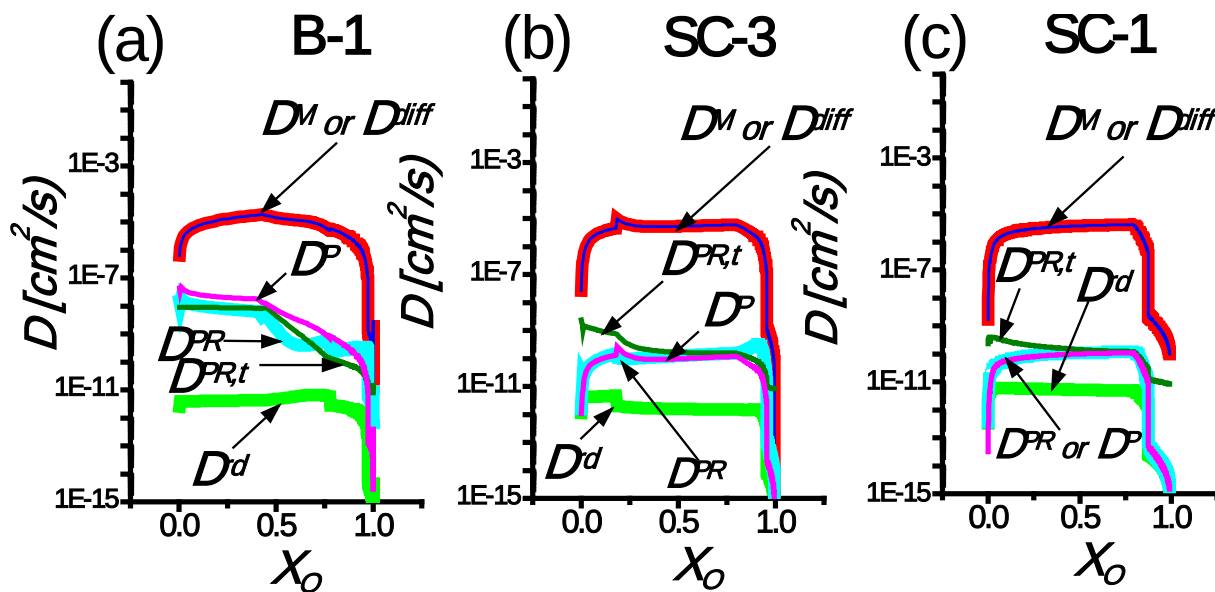


Fig. 9: Diffusion coefficients for the batch process B-1, and the semicontinuous SC-3 and SC-1.

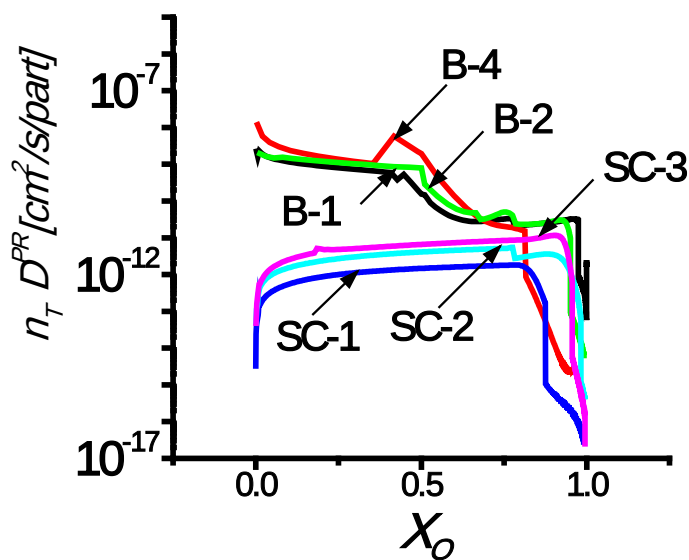


Fig. 10: Global diffusion of the radicals in the particle indicated by the product $n_T D^{\text{PR}}$ for the batch processes B-1, B-2 and B-4 and the semicontinuous processes SC-1 to SC-3. All this processes with the same feed composition.

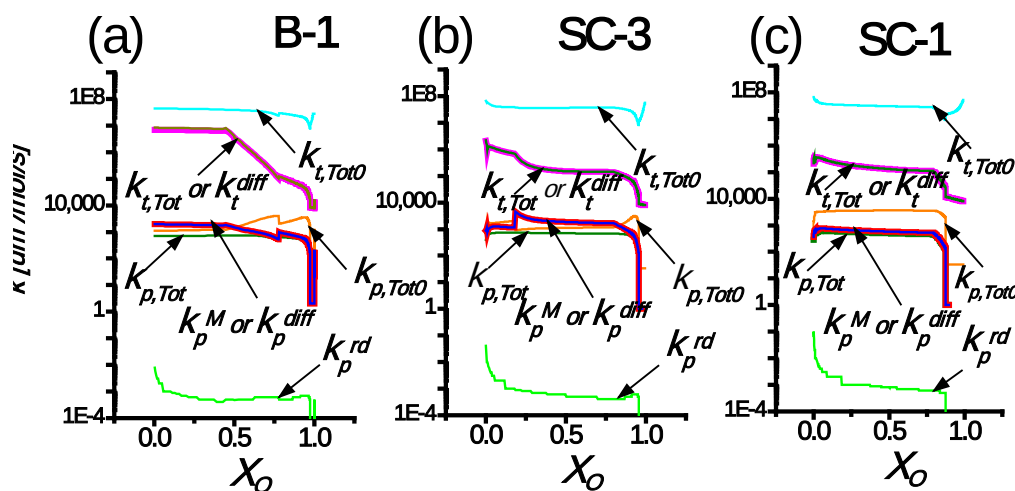


Fig. 11: Propagation and termination rate coefficients for the batch process B-1, and the semicontinuous SC-3 and SC-1.

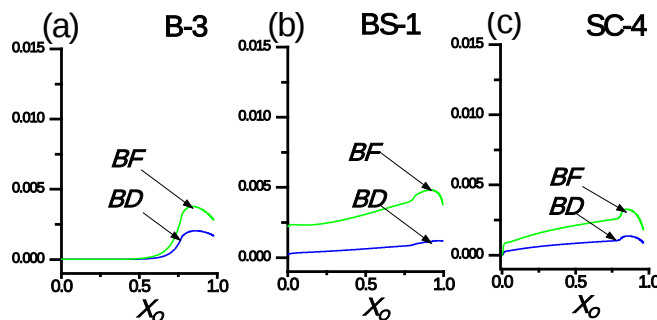


Fig. 12: Average branching density BD and branching fraction BF: a. batch B-3, b. seeded process BS-1, and c. semicontinuous SC-4.

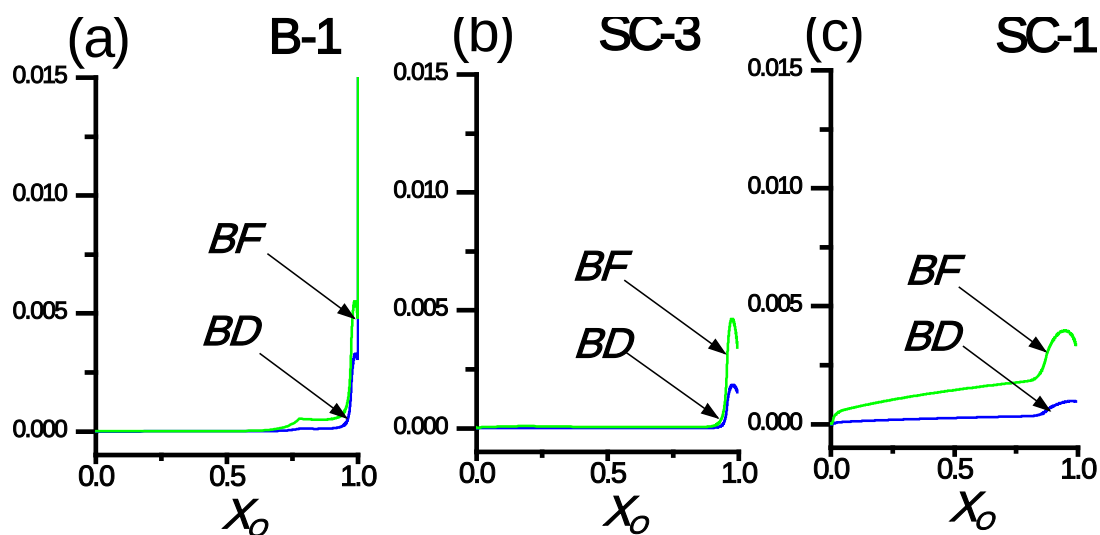


Fig. 13: Average branching density BD and branching fraction BF for: a. batch B-1, b. semicontinuous process SC-3, and c. semicontinuous process SC-1. The processes are ordered in accordance to higher addition rate of monomers from left to right.

Table 1: Kinetic rates of polymer radicals backbiting.

Units	Equations	Comments
n_{cbb} #·rad/part	$\frac{dn_{cbb}}{dt} = R_{ncbb}(P_{ijk}) - R_{p,ncbb} - R_{t,ncbb} - R_{m,ncbb} - R_{T,ncbb}$ $= R_{ncbb}(P_{ijk}) - \Sigma R_r$ $n_{cbb,t} = n_{cbb,t-\Delta t} + \left(\frac{dn_{cbb}}{dt} \right)_{t-\Delta t} \Delta t$ $R_{ncbb} = K_{cbb} (f_{a,bb} P_{ijk}(c,a,c) + f_{b,bb} P_{ijk}(c,b,c) f_{ab} + f_{c,bb} P_{ijk}(c,c,c))$ $\frac{(n_{t-3\Delta t} n_{t-2\Delta t} n_{t-\Delta t})}{3}$ $P_{ijk}(i,j,k) = \frac{n_{i,t-3\Delta t}}{n_{t-3\Delta t}} \frac{n_{j,t-2\Delta t}}{n_{t-2\Delta t}} \frac{n_{i,t-\Delta t}}{n_{t-\Delta t}} \quad \text{with } i,j,k = a, b, c$ $R_{p,ncbb} = \sum_i k_{p,cbbi} n_{cbb} [M_i]_p \quad \text{with } i = a, b, c$ $R_{t,ncbb} = k_{t,cbb} \frac{n_T^2}{v_p} \frac{10^3}{N_A}$ $k_{t,cbb} = \frac{1}{n_T^2} (n_{cbb}^2 k_{t,cbb} + \sum_{j,j \neq cbb} 2n_{cbb} n_j k_{t,cbb,j})$ $\text{with } j = a, b, c$ $R_{m,ncbb} = \sum_i k_{p;cbbi,0} C_{m,cbbi} n_{cbb} [M_i]_p$ $\text{with } i = a, b, c$ $j = a, b, c$	This work (TW). It was taken into account the penultimate effect in the rate of backbiting R_{ncbb}, in which the factors of styrene and methyl methacrylate as penultimate monomers in the polymer radical are $f_{a,bb} = 0.6$ and $f_{b,bb} = 0.6$, respectively. For the monomers of BuA $f_{c,bb} = 1$ [5]. The j-ended radicals are St = a, MMA = b, secondary radicals of BuA = c and tertiary electrophilic radicals of BuA = cbb. The monomers are: St = a, MMA = b, BuA = c. The crossed terms are the geometric mean of the individual parameters. The transfer constants of the BuA tertiary electrophilic radicals $C_{m,ncbbi}$ and $C_{T,ncbb}$ were taken equal to the secondary radicals of BuA. The gel effect was taken into account in $R_{p,ncbb}$, $R_{T,ncbb}$, $R_{t,ncbb}$ and
	$R_{T,ncbb} = k_{p;cbbi}, C_{m,cbbi,T} n_{cbb} [M_T]_p$	$R_{m,ncbb}$ in a similar way to the kinetic rates of the other radicals.

Table 2: Equations used to evaluate the gel effect of the polymerization rate constant k_p of the *BuA*-ended radicals (dm³/mol) [12].

1. Before $X_{vfc2} = 0.84$, $j = c, cbb$.

$$k_{p,ji} = \frac{k_{p,jj0}}{r_{ji}} \exp[-A_{1kj}(\frac{1}{V_f} - \frac{1}{V_{fc1kj}})] \quad k = 1,2$$

$$k_{p,ji} = \frac{k_{p,jj0}}{r_{ji}} \exp[-A_{1kj}(W_p - W_{pc1kj})] \quad k = 3$$

2. After the critical value $X_{vfc2} = 0.84$; $j = c, cbb$

$$k_{p,ji} = \frac{k_{p,jj0}}{r_{ji}} \exp[-A_{2kj}(\frac{1}{V_f} - \frac{1}{V_{fc1kj}})] \quad k = 1,2$$

$$k_{p,ji} = \frac{k_{p,jj0}}{r_{ij}} \exp[-A_{2kj}(W_p - W_{pc1kj})] \quad k = 3$$

Batch B-3.

$$k_{p,ji} = \frac{k_{p,jj0}}{r_{ji}} \exp[-A_{1kj}(\frac{1}{V_{fc2kj}} - \frac{1}{V_{fc1kj}}) - A_{2kj}(\frac{1}{V_f} - \frac{1}{V_{fc2kj}})] \quad k = 1,2$$

$$k_{p,ji} = \frac{k_{p,jj0}}{r_{ji}} \exp[-A_{1kj}(W_{pc2kj} - W_{pc1kj}) - A_{2kj}(W_p - W_{pc2kj})] \quad k = 3$$

- We consider that the gel constants and critical values of V_f and W_p are equal for the secondary and tertiary radical of *BuA*.
- The monomers are indicated by “i” and the kind of k_p -gel model by “k”.

Table 3: Kinetic constants for k_p -gel effect Equations used in the simulation model.

	Hamielec		Ray		Wp		h = 1 Before, h = 2 After
	A_{h1}	V_{fch}	A_{h2}	V_{fch}	A_{h3}	W_{pch}	
<i>St</i>	0.015	0.07	10.50	0.07	1.62	0.67	k_p - k_t average model [12]
<i>MMA</i>	0.015	0.07	10.50	0.07	1.62	0.67	k_p - k_t average model [12]
<i>BuA</i>	0.05	0.10	24.24	0.10	3.75	0.48	k_p - k_t average model [12]
	0.350	0.14	40.00	0.14	5.74	0.19	Before $X_{vfc2} = 0.84$ ($W_{pc2} = 0.7945$), TW.
	0.11	0.14	21.91	0.14	3.65	0.19	After $X_{vfc2} = 0.84$ ($W_{pc2} = 0.7945$), almost all processes, TW.
	0.11	0.05	21.91	0.05	3.65	0.80	After $X_{vfc2} = 0.84$ ($W_{pc2} = 0.7945$); Only B-3, TW.

Table 4: Sequence for the evaluation of the diffusion coefficients in the polymerization reaction^a (From left to right).

1 $\frac{1}{k_p^{diff}} = \frac{1}{k_{p,Tot}} - \frac{1}{k_{p,Tot0}}$ $k_{p,Tot} = \frac{\sum_{i,j}^c k_{p,ji} n_j [M_i]_p}{n_T [M_T]_p}$ $k_{p,Tot0} = \frac{\sum_{i,j}^c k_{p,ji0} n_j [M_i]_p}{n_T [M_T]_p}$ $k_p^{diff} = k_p^{rd} + k_p^M$ $k_p^{rd} = 4 \pi \frac{n_T}{[M_T]_p v_p} D^{rd} \left(\frac{\sigma_{LJ}^M}{2} + \frac{\sigma_{LJ}^R}{2} \right)$ $D^{rd} = k_{p,Tot} [M_T]_p \frac{a_{PR}^2}{6}$ $a_{PR}^2 = \sum_{j=a}^c X_j \left(\left[\frac{\langle r_0^2 \rangle_j}{N_i} \right]^{1/2} \right)^2$ $\sigma_{LJ}^R = \frac{\sum_{j=a}^{cbb} n_j \sigma_j^R}{n_T}$ $\sigma^M = \frac{\sum_{i=a}^c [M_i]_p \sigma_i^M}{[M_T]_p}$ $k_p^M = k_p^{diff} - k_p^{rd}$ $k_p^M = 4 \pi \frac{n_T}{[M_T]_p v_p} D^M \left(\frac{\sigma_{LJ}^M}{2} + \frac{\sigma_{LJ}^R}{2} \right)$	2 $D^M = \frac{k_p^M [M_T]_p v_p}{4 \pi n_T \left(\frac{\sigma_{LJ}^M}{2} + \frac{\sigma_{LJ}^R}{2} \right)}$ On the other hand, $\frac{1}{k_t^{diff}} = \frac{1}{k_{t,Tot}} - \frac{1}{k_{t,Tot0}}$ $k_{t,Tot}$ and $k_{t,Tot0}$ are given in Table S-2 (Supporting Information). $N^P = \frac{v_1}{v_0}$ $N^{PR} = \frac{\mu_1}{\mu_0}$ $c^* = \frac{3 N^P PM_{aver}}{4 \pi N_A R_g^3}$ $PM_{aver} = \sum_{j=a}^c X_j PM_j$ $R_g = \left(\frac{a_{PR}^2 N^P}{6} \right)^{1/2}$	3 Vg. For condition 2 in B-1 $n_1 = n_3 = 0.75$, $n_1 = n_2 = 1.59$ $N^{PR,t} = \left(\frac{D^M}{\left[\frac{1000 k_t^{diff}}{8 \pi N_A \left(\frac{\sigma_{LJ}^R}{2} + \frac{\sigma_{LJ}^R}{2} \right)} - D^{rd} \right] c^{n_i}} \right)^{(1/n_j)}$ Iteration in the values of n_0, n_1 and n_2 until finding a distribution of $N^{PR,t}$ similar a N^{PR}. Evaluation of the values of $D^{PR,t}$ in Equation (9bi)-(9biii). Substitution of $N^{PR,t}$ by N^{PR} and N^P in order to evaluate D^{PR} and D^P (without D^{rd}), respectively. As reference is calculated $D^{PR,1,2}$ with $n_1 = 2$ and $n_2 = 2$. $D^{com,P,2} = D^{P,2} = \frac{D^M}{(N^P)^2}$
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a. The subindex "i" for the monomers, subindex "j" for the j-ended radicals.

Table 5: Exponents of the degree of polymerization^a of the radicals associated to the termination $N^{PR,t}$ in order to fit the degree of polymerization of the radicals N^{PR} .

	B-1	B-2	B-3	B-4	SC-1	SC-2	SC-3	SC-4
n_0	1.40	1.40	1.40	1.40	-	-	-	-
n_1	1.40	1.50	1.47	1.60	-	-	-	-
n_2	1.59	1.62	1.72	1.41	1.85	1.78	1.78	1.89
Conditions ^b	0,1,2,4 Almost 2	0,1,2	0,1,2	0,1,2 Almost 2	2,4 Almost 2	2,4 Almost 4	4	1,2,4 Almost 2
Range W_p ^c	0.48-0.96	0.48- 0.97	0.45- 0.92	0.47- 0.96	0.79- 0.82	0.80- 0.91	0.62- 0.82	0.74- 0.89

- a. $n_3 = 0.75$, $n_4 = 1.75$ (See Text).
 b. See Equation (9).
 c. In the semicontinuous processes, the increment of W_p at almost zero of conversion is not considered.

Table 6: Experimental and simulated range of the transition of T_g , ΔT_g , for the batch and semicontinuous processes.

	B-1	B-2	B-3 ^b	SC-1	SC-2	SC-3	SC-4
ΔT_g (°C) Experimental.	19-70	25-55	20-44	29-61	27-69	27-63	12-23
k_p-k_t average model							
$\Delta T_{g,DSC}$ (°C)	9-70	32-70	12-42	67-70	46-64	59-64	9-32
$\Delta T_{g'}^a$ (°C)	9-70	32-70	-24-42	67-68	45-62	59-62	9-29
Backbiting model							
$\Delta T_{g,DSC}$ (°C)	9-70	17-70	16-42	60-69	45-60	59-65	21-32
$\Delta T_{g'}^a$ (°C)	9,-70	17-70	-24-42	58-61	45-61	59-63	4-23

- a. For the semicontinuous processes the higher value of the range of T_{gi} was obtained by the intersection of the tangent to the curve of T_{gi} versus X_O at the beginning of the reaction and the tangent when the conversion goes from 10 to 30 wt%.
 b. It was difficult to define the onset of the experimental T_g of B-3.

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