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# Branching and Crosslinking in Emulsion Polymerization

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**Summary:** The seeded semibatch emulsion polymerization of butyl acrylate (BA) with allyl methacrylate (AMA) and butanediol diacrylate (BDA) was used to study the influence of the crosslinkers on the kinetics, branching and crosslinking density, gel fraction and sol MWD produced during the experiments carried out at 80°C using potassium persulfate as initiator. Surprisingly, the most reactive crosslinker, BDA, produced the less crosslinked, branched and gel containing polymer. These results were explained with the help of a mathematical model in terms of cyclization reactions and diffusion controlled propagation and termination reactions.

**Keywords**: branching; butyl acrylate; crosslinking; cyclization; diffusion controlled mechanisms; gel polymer; mathematical modeling

## Introduction

Multifunctional monomers, often known as crosslinkers, are usually employed in free-radical polymerization to produce homopolymers or copolymers (when polymerized with other vinylic monomers) that lead to polymer networks with applications in medicine, pharmaceuticals, paints, column packing, optics, polymer additives, ion exchange resins and diene rubber products. When used in emulsion polymerization, crosslinkers allow to control particle morphology, produce monodisperse polymer particles, enhance mechanical properties of latexes used for paints and coatings and produce impact modifiers or polymeric additives for other polymeric matrices.

The works reporting in the open literature about the kinetics and the microstructural properties of the polymers produced in the emulsion copolymerization of vinylic monomers with crosslinkers are scarce. In addition, batch experiments, which are rarely employed in industry, are often used and the amount of crosslinker employed exceeds that used in commercial practice [1-9]. On the

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other hand, considerable efforts have been devoted to the development of models for branching and crosslinking formation in nonlinear emulsion polymerization. Mean-field theory based models have been predominantly used [10-15] although Monte-Carlo techniques[16-18] and methods based on the kinetics of gelation [19] have more recently emerged as an alternative to predict branching and crosslinking in nonlinear polymerization.

In this work, the effect of two crosslinkers on the kinetics of the seeded semibatch emulsion polymerization of BA and on the microstructural properties (branching, crosslinking, gel formation and sol MWD) of the resulting polymer was investigated. The crosslinkers used were allyl methacrylate (AMA) and butanediol diacrylate (BDA), both regularly employed as crosslinking agents in industry. The experimental results were analyzed by means of a mathematical model previously developed for the emulsion polymerization of BA [13] that was conveniently modified to account for the presence of the crosslinking comonomer and the additional branching and crosslinking reactions that occur in this copolymerization.

## Experimental

Technical grade butyl acrylate (Quimidroga S.A.), sodium lauryl sulfate (SLS, Merck), sodium hydrogen carbonate ($NaHCO_3$Panreac), disodium hydrogen phosphate ($Na_2HPO_4$, Panreac), potassium persulfate (Fluka), allyl methacrylate (Aldrich) and butanediol diacrylate (Atofina) were used as received. All polymerizations were carried out using double deionized water (DDI). The seed was prepared in batch at 60 °C using the formulation of Table 1. The semicontinuous experiments were carried out at 80°C with the formulation shown in Table 2 in a 1L jacketed reactor agitated with a three blade impeller at 200 rpm and using a feeding time of 3h. Each crosslinker was used at two different concentrations, 0.23 and 2.3% based on the total number of moles of BA. Moreover, for comparison purposes, a reference experiment was performed without crosslinker, namely, a homopolymerization of BA.

Table 1. Recipe used for the seed preparation.

| | |
|---|---|
| Butyl acrylate (g) | 350.5 |
| Water (g) | 900 |
| SLS (g) | 7.0 |
| $NaHCO_3$ (g) | 1.75 |
| $K_2S_2O_8$ (g) | 1.77 |

Table 2. Recipe used for the semicontinuous emulsion copolymerization of BA/crosslinkers

| | Initial charge | Stream 1 | Stream 2 | Total |
|---|---|---|---|---|
| Seed (g) | 20.8 | | | 20.8 |
| Water (g) | 85 | 410 | 23.25 | 518.25 |
| SLS (g) | 0.17 | 2.86 | | 3.03 |
| $Na_2HPO_4$(g) | | 1.29 | | 1.29 |
| Butyl acrylate (g) | | 234 | | 234 |
| Crosslinker (g) | | 0.23%-2.3% | | |
| $K_2S_2O_8$ (g) | 0.155 | | 0.55 | 0.705 |

During the polymerization, samples were withdrawn from the reactor at regular sampling times and analyzed to measure the gravimetric conversion, the branching density, the gel content, the sol MWD and the swelling (which gives an indirect indication of the crosslinking density). Branching density was measured by $^{13}C$ NMR using a Bruker DPX 300 apparatus with a BBO probe operating at 75.5 MHz. Gel content was measured by means of an extraction process in THF under reflux conditions. Sol MWD was measured in a GPC apparatus equipped with a dual detector (refractive index and viscosity, VISCOTEK Model 250) and three columns (Styragel HR2,HR4 and HR6) at 35 °C using THF as carried fluid at 1 mL/min. Swelling experiments were carried out in methyl ethyl ketone, MEK, during 24 hours at ambient temperature. Swelling was calculated as the ratio between the weight of the swollen gel polymer and the weight of the gel polymer. The average error associated with these techniques is ±3% for gel content, ±7% for swelling, and ±9% for branching density. Additional details on the measurements of branching, gel content and sol MWD can be found elsewhere [20,21].

The chemical structure of the two crosslinkers is shown in Figure 1. AMA is an asymmetrical divinyl monomer containing a methacrylic double bond and an allylic double bond. BDA is a symmetrical divinyl monomer with two acrylate double bonds. In terms of the reactivity of these double bonds, the methacrylic is more reactive than the acrylic, which is much more reactive than the allylic [22].

Figure 1. Chemical structures of allyl methacrylate (AMA) and butanediol diacrylate (BDA).

## Results and Discussion

Figure 2 shows the instantaneous conversion for the polymerizations carried out without and with crosslinkers at the different concentrations. After the initial stages of the process in which some monomer accumulation was observed, the process evolved under rather starved conditions (namely, the instantaneous conversions was greater than 90%). Furthermore, the addition of either BDA or AMA did not significantly affect the kinetics.

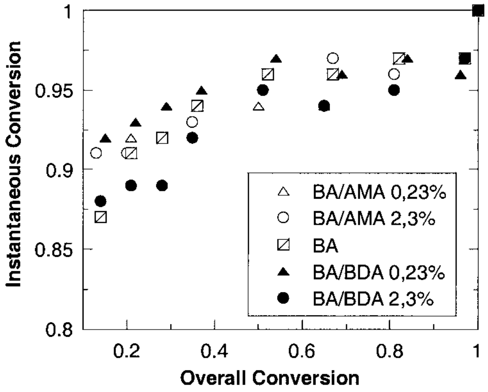

Figure 2. Conversion evolution of the instantaneous conversion in the seeded semibatch experiments of BA/crosslinkers.

Figure 3 presents the evolution of the branching density as measured for the experiments carried out with 2.3% of AMA and BDA. For the sake of comparison, this figure also includes the branching measured in the absence of the crosslinking monomers. It is worth explaining that the branching density reported in the plot corresponded to the quaternary carbons measured from the spectra [20,21] (at 48-49 ppm). Intermolecular and/or intramolecular (backbiting) chain transfer to polymer reactions form this quaternary carbon. As shown by Plessis et al. [21,23,24], in the homopolymerization of BA most of the branches are short branches formed by backbiting. The copolymerization of BDA and AMA does not yield either new branching ($C_q$) points or new sites prone to suffering H abstraction that upon propagation will lead to a quaternary branch point. However, AMA contains a quaternary carbon in the methacrylic group, but fortunately the chemical shift of this group (44-45 ppm) does not perturb the determination of the branches formed by the chain transfer to polymer. Note also that the crosslink points (tetrafunctional or H shaped structures) produced with these crosslinkers do not form quaternary carbons and hence these branches were not accounted for in the data plotted in Figure 3.

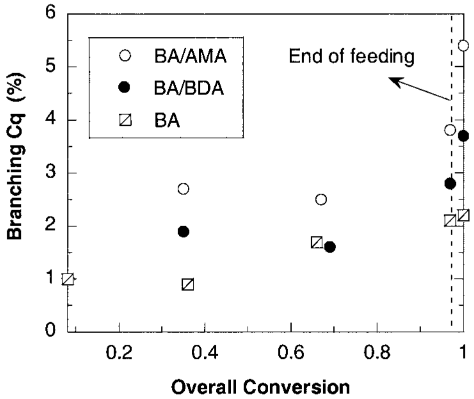

Figure 3. Evolution of the branching density for the semibatch emulsion copolymerization reactions carried out with 2.3 mol% of AMA and BDA.

There are important features in this plot to be discussed. First, the level of branching in the experiments with crosslinker was higher than in the absence of crosslinker, even though as pointed out above the copolymerization of the crosslinker should not directly produce more branching. Second, an important increase of branching density during the cooking period was observed: in approximately 3% monomer conversion, branching increased from 2.7 to 3.8% for BDA and from 3.9 to 5.3% when AMA is used. Plessis et al· [20-21,23-24] reported that backbiting was the predominant branching mechanism in the polymerization of BA. We believe that it is also predominant during the copolymerization. However, during the cooking period, the amount of monomer remaining was not enough as to justify this increase, and hence other mechanism should be responsible for the additional branching. Third, the branching density was higher for

AMA than for BDA and the increase during the cooking was also more important for AMA. Although not shown, in experiments with a lower concentration of crosslinker (0.23%), the branching density obtained with these crosslinkers was similar (2.9 and 3% for BDA and AMA, respectively), but still higher than for the homopolymerization of BA.

Figure 4 and Table 3 show the evolution of gel content for the experiments carried out with a 0.23mol% of crosslinker and the final gel content for all the experiments, respectively. The amount of gel was greater for the experiments carried out with crosslinker than for the homopolymerization of BA.

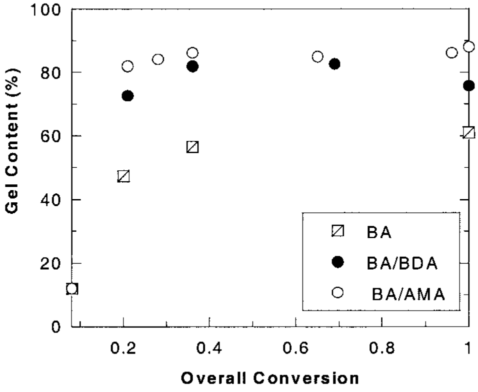

Figure 4. Evolution of the gel content for the semibatch emulsion copolymerization reactions carried out with 0.23mol% of AMA and BDA.

Note that in the homopolymerization of BA, gel was mainly formed by the intermolecular chain transfer to polymer plus the bimolecular termination by combination [13,20,21] (propagation to pendant/terminal double bonds formed by chain transfer to monomer did not contribute much because of the low amount of pendant/terminal double bonds formed at the low monomer concentrations existing in the polymer particles). However, when the divinylic monomers were used, the crosslinking reaction (propagation to the pendant double bond of the divinylic monomer) was predominant and the gel was mainly due to crosslinking. For the experiments carried out with 2.3mol% of crosslinker, the evolution gel content was rather similar for both crosslinkers (slightly greater for AMA, Table 3). This was not expected because the pendant double bond of BDA (acrylate) is more reactive than that of the AMA, that is an allylic double bond [22].

Table 3. Gel content (using THF) of the final latexes produced in the semibatch experiments.

| | Gel content (%) |
|---|---|
| BA | 60 |
| BA/BDA(0.23%) | 76 |
| BA/BDA (2.3%) | 89 |
| BA/AMA (0.23%) | 88 |
| BA/AMA (2.3%) | 90 |

Figure 5 and Table 4 display the evolution of the swelling for the latexes obtained with 2.3% crosslinker and the swelling values for all the final latexes, respectively. Table 4 also shows the gel content measured in the swelling experiment. Note that during the swelling experiments the amount of gel is also measured and reported in Table 4. These values do not have to necessarily match with the gel fractions reported in Figure 4 and Table 3 because the extractions were carried out with a different solvent and at different conditions. The swelling value of a polymer is inversely proportional to the crosslinking density [25], namely the more crosslinked the polymer, the less its swelling capability. Figure 5 shows that the latexes prepared with the crosslinkers were more crosslinked (lower swelling value) than the homopolymer of BA. In addition, latexes with AMA were more crosslinked than the latexes with BDA. This seems contradictory because of the higher reactivity of the pendant double bond of the BDA. The swelling evolution reveals that the crosslinking density evolved in a different manner for the both crosslinkers. Whereas at the beginning of the process (conversion ca. 20%) and during the plateau period (conversions up to 80%), the copolymer with BDA was more or equally crosslinked than that with AMA, and at the end of the process the crosslinking density of the polymer containing AMA was greater. This trend was accelerated during the cooking period, in which the crosslinking density significantly increased for the copolymer produced with AMA, whilst for the BDA there was not additional change. This evolution suggests that: a) BDA reacted faster; b) BDA used some bonds in reactions that did not yield effective crosslinking; and c) there were no BDA double bonds available during cooking. A possible explanation to this result is that primary cyclization [1,10,26] (intramolecular crosslinking reaction) is more important for BDA than for AMA. This intramolecular crosslinking reaction, as shown in Figure 6, forms cycles or loops which are not elastically efficient and hence they do not contribute in the polymeric network. Therefore, the efficient crosslinking density is reduced [27] and the swelling increases.

Table 4. Swelling values (in MEK) of the final latexes produced in the semibatch experiments.

| | Crosslinker (mol%) | Swelling(-) | Gel content (%) |
|---|---|---|---|
| BA | | 22.8 | 83 |
| BA/AMA | 0.23 | 11.5 | 91 |
| BA/AMA | 2.3 | 5.4 | 97 |
| BA/BDA | 0.23 | 16.5 | 84 |
| BA/BDA | 2.3 | 10.6 | 91 |

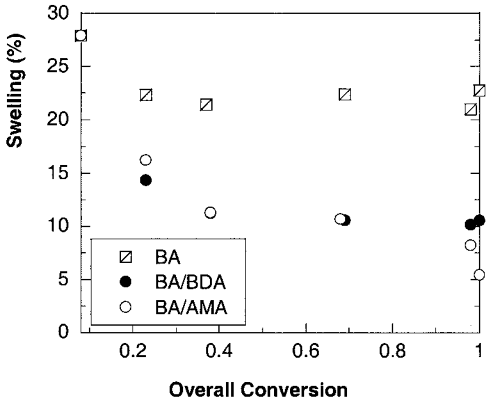

Figure 5. Evolution of the swelling value for the semibatch emulsion copolymerization reactions carried out with 2.3mol% of AMA and BDA.

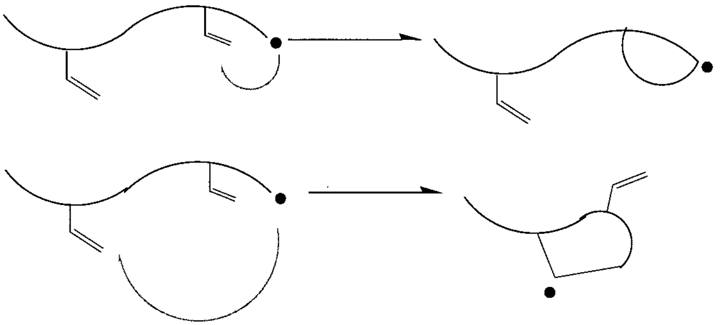

Figure 6. Intramolecular crosslinking reactions (primary cyclization).

Finally, Figure 7 presents the sol molecular weights of samples taken during the experiments. Note that the sol polymer injected to the GPC was recovered from the swelling experiments. Interestingly, the sol molecular weight of the BA/AMA copolymer was initially higher (in agreement with the lower crosslinking density), but then decreased faster than in the case of BA/BDA. At the end of the process, the sol molecular weight for the BA/AMA copolymer was lower than that prepared with BA/BDA. It is also noticeable that the sol molecular weight for the BA homopolymer was more larger than those of the polymers containing crosslinkers.

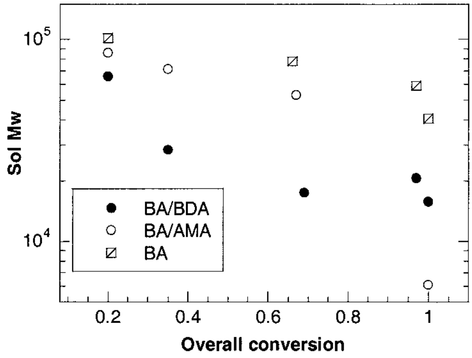

Figure 7. Time evolution of the sol weight average molecular weight for the semibatch emulsion copolymerization reactions carried out with 2.3 mol% of AMA and BDA.

All the experimental results presented above show an unexpected trend. Indeed, one would expect that the most reactive crosslinker, BDA, would produce a polymer with a higher gel content, a more crosslinked network and hence lower sol molecular weights. Based on the assumption that most branches are formed by backbiting, the branching density was expected not to be dependent on the crosslinker used, but the experimental results showed that the copolymers containing AMA were significantly more branched.

The results were analyzed with a mathematical model previously developed for the homopolymerization of BA [13] and successfully extended to the copolymerization of BA with styrene [28]. The model was updated to account for the specific kinetic features of a divinylic monomer such as BDA and AMA. It is out of the scope of this paper to fully describe the model, but it is worth explaining the kinetic events that were considered in the model to correctly compute the branching and crosslinking density.

Since the experimental branching density corresponded to the quaternary carbons measured by $^{13}$C NMR, the model calculated the branching density accounting for the reactions that led to quaternary carbons. These mechanisms did not change by the presence of the crosslinker, and hence they were the same as in the original models [13, 28]; namely, intermolecular chain transfer to polymer and backbiting.

Crosslinking units were computed as the number of propagation events to pendant double bonds of the divinylic monomer plus the number of termination events by combination of two branched polymer radicals, plus the number of propagation events of branched polymer radicals on terminal double bonds formed by chain transfer to monomer. Each of these reactions created two crosslinking points (trifunctional unit).

In addition, primary cyclization or intramolecular cyclization and secondary cyclization or intermolecular cyclization were considered [33] (Figure 6). The later effectively contributes to the elastic properties of the network and within the framework of the mean field theory used in our mathematical model, there was not difference with the regular crosslinking reactions considered. On the other hand, primary cyclization is a way of using pendant double bonds without contributing to the network formation.

In highly crosslinked systems, the reactivity of functional groups and free-radicals becomes diffusionally limited [30,31] being significantly more important than ordinary diffusion that usually causes the gel effect. Under such extreme diffusional limitations, trapping of radicals and severe reaction-diffusion (the movement of the radical is only due to the propagation of the chain) are events that control the development of the network formation and the crosslinking kinetics. Under these conditions clusters (or microgels) are formed and this favors cyclization reactions [32].

In order to incorporate diffusion control into the model the additional diffusional limitations, due to the highly crosslinked structure of the polymerization medium, were accounted for in a semiempirical way. Thus all propagation, transfer to small molecules and termination by combination reactions were reduced by a function that depends on the crosslinking density as follows:

$$k_p = k_{p0}\, f(\rho) ; k_p^* = k_{p0}^*\, f(\rho) ; k_{tr,X} = k_{tr,X0}\, f(\rho)$$

$$k_t = k_{t0} \left[ f(\rho) \right]^2$$

where $k_p$ and $k_{p0}$ are propagation rate constants, $k_p$* and $k_{p0}$* are propagation to pendant double bonds, $k_{trX}$ and $k_{trX0}$ chain transfer to X molecules and $k_t$ and $k_{t0}$ bimolecular termination rate constants. The subscript 0 in these rate constants indicates no diffusional limitation.

The mechanism of backbiting does not require the displacement of the whole chain, and hence it was considered that it was not affected by diffusional limitations.

Primary cyclization was included as an additional reaction in the kinetic scheme. Although as shown in Figure 6, primary cyclization can occur within the same divinylic monomer molecule or in other pendant double bond of the same molecule, the first mechanism is favored because the formation of shorter cycles is energetically less demanding [33]. Primary cyclization does not require the movement of the whole chain, and hence it was considered that it was not affected by diffusional limitations.

The reactivity ratios used in the simulation were taken from the literature [22,29], and are presented in Table 5. As it can be seen the methacrylic double bonds are more reactive than acrylate ones, and these more reactive than allylic double bonds. For the BA/BDA system, the reactivities of all double bonds were considered to be the same. In the simulations, the same reactivity for pendant and ordinary double bonds was used, namely $k_p/k_p^*=1$.

Table 5. Reactivity ratios of the double bonds involved in the polymerizations[22,29].

| Double bond | Acrylate | Allyl | Methacrylic |
|---|---|---|---|
| Acrylate | - | 11.7 | 0.414 |
| Allyl | 0.04 | - | 0.024 |
| Methacrylic | 2.24 | 41 | - |

Figure 8 shows the simulated branching density for the copolymerization of BA/BDA at 2.3mol% when the diffusional limitations were included in the model. It can be seen that branching density increased considerably because the chain transfer to polymer mechanisms (predominantly backbiting) was favored over propagation and termination of growing chains, and hence the branching density increased.

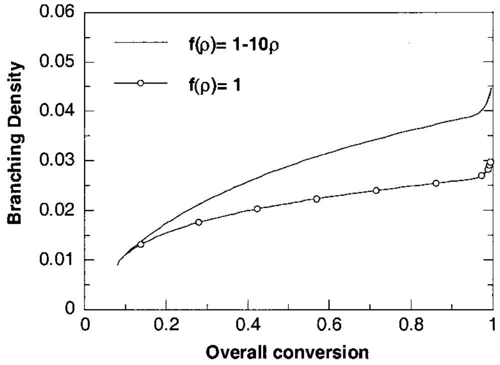

Figure 8. Evolution of the simulated branching density for the semibatch emulsion copolymerization of BA/BDA at 2.3 mol%.

Figure 9 shows the simulated effect of the cyclization constant ratios, $K_{cl}$, on the crosslinking density for the copolymerizations with BDA and AMA. To simulate these experiments, $K_{cl}$ was taken from the data reported by Matsumoto et al.[34] for allyl methacrylate because no information was found for BDA.

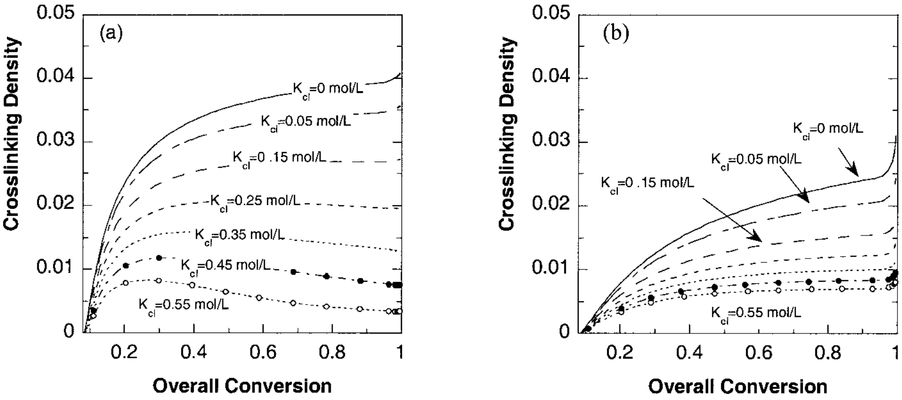

Figure 9. Evolution of the simulated crosslinking density for the copolymerization of BA with the crosslinkers with different cyclization constant ratios: a) BA/BDA; b) BA/AMA.

It is worth noting that the cyclization constant ratio $K_{cl}$ (mol/L) is a ratio between two propagation rate constants; that of the cyclization reaction (intramolecular propagation within the divinylic monomer, $k_{cl}$, and the propagation rate constant to the monomer, $k_{p0}$. Whereas primary cyclization led to a noticeable reduction on the crosslinking density of BA/BDA copolymers, its effect is less important for the BA/AMA copolymer. The different behavior of both crosslinkers for the same cyclization ratio is due to the important difference of the intramolecular propagation rate constant of the radical to the pendant double bond that makes the cyclization reaction to be much less important for the AMA system than for the BDA; e.g. for $K_{cl}$=0.25 the cyclization rate constant is 131 $s^{-1}$ for AMA, whereas for BDA is $1.34x10^4$ $s^{-1}$. This explains why we found that the crosslinking density was higher for AMA than for BDA in the semibatch emulsion polymerization. It is also noticeable that simulation predicted that during the cooking period there was not an increase in the crosslinking density for BDA, but an important one for AMA, which was due to the late consumption of unreacted allylic double bonds as it is shown in Figure 10.

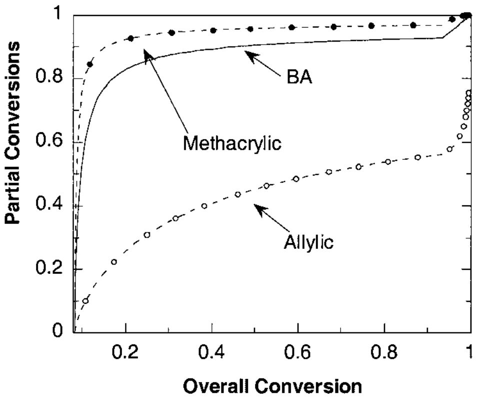

Figure 10. Evolution of the partial conversions of the different double bonds in the semibatch copolymerization of BA/AMA at 2.3 mol%.

This plot agrees well with the experimental evidence that during the process no methacrylic double bonds could be detected neither by $^{13}C$ or $^{1}H$ NMR, but allylic double bonds were detected.

An indirect way of assessing that the diffusional limitations and the primary cyclization are responsible for the observed results is to perform simulations with a mathematical model in which these mechanisms were not included. Figure 11 shows the simulated branching and crosslinking density for the experiments carried out with 2.3% of BDA and AMA as crosslinkers. The plot shows that contrary to what it was obtained experimentally, the simulated crosslinking density was higher for the copolymer with BDA. This evolution was a consequence of the relative consumption of the double bonds. Allyl methacrylate copolymerized with BA through the methacrylic double bond, and the allylic remained pendant. Only when BA was almost depleted, the allylic double bond reacted, which led to an increase in the crosslinking density during the cooking period, but still not enough as to yield crosslinking density higher than for BDA. Notice that for BDA this increase was not predicted because most of the double bonds reacted before the cooking period. Nevertheless, in this case each unreacted BDA pendant double bound contributes to the effective crosslinking and hence a higher crosslinking density was achieved.

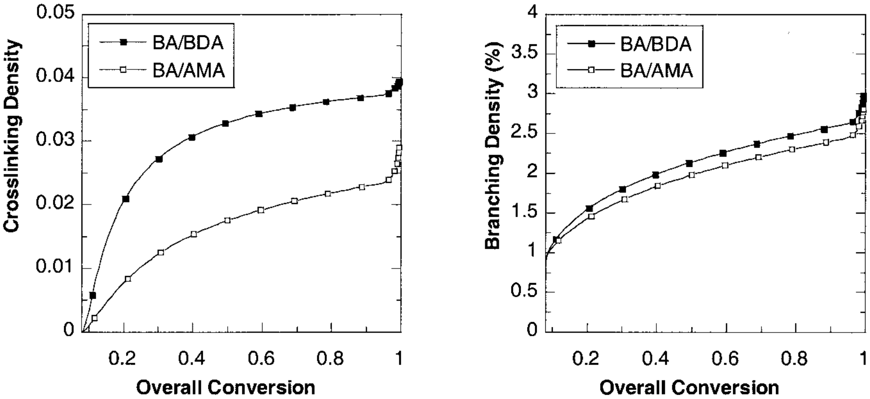

Figure 11. Simulated evolution of the crosslinking and branching density for the semibatch experiments carried out with the crosslinkers at 2.3 mol%. Neither cyclization nor diffusional limitations were considered.

The simulated branching density was slightly higher for the copolymer with BDA because of the higher instantaneous conversion, that as shown by Plessis et al. [20,21,28] favored backbiting over propagation and hence produces more branches.

The results presented above strongly suggest that the diffusional limitations caused by the highly crosslinked structure together with primary cyclization were the origin for the differences observed in the experiments carried out with AMA and BDA.

## Conclusions

The effect of two crosslinkers (allyl methacrylate and butanediol diacrylate) on the kinetics of the seeded semibatch polymerization of BA and on the microstructural properties of the polymers was studied. The results showed that the addition of the crosslinkers did not have an effect on kinetics. On the other hand, branching, crosslinking and sol molecular weights were strongly affected, by the choice of the crosslinker. Surprisingly, the most reactive crosslinker (BDA) produced the less crosslinked polymer. Furthermore, the branching density was higher in the presence of crosslinker, and AMA produced the most branched polymer. These unexpected results were semiquantitatively explained with the help of a mathematical model of the process. Severe diffusional limitations due to the presence of a highly crosslinked polymer, as well as intramolecular crosslinking reactions (primary cyclization) allowed explaining the higher crosslinking density achieved for the copolymers with AMA.

## Acknowlegdements

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