Seeded Semicontinuous Emulsion Copolymerization of Butyl Acrylate with Cross-Linkers†

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ABSTRACT: The seeded semicontinuous emulsion copolymerization of butyl acrylate (BA) with divinyl monomers (butanediol diacrylate, BDA, and allyl methacrylate, AMA), at 80 °C and using potassium persulfate as initiator was investigated. Particularly, the study of the influence of the type and amount of cross-linkers on the kinetics, level of branching, cross-linking density, gel fraction, sol molecular weight, and latex film mechanical properties (i.e., glass transition temperature, T_g, storage modulus, and molecular weight between entanglements, M_e) produced during the polymerizations was considered. The results showed that the most reactive cross-linker, BDA, produced the less cross-linked, branched, and gel-containing polymer. Mechanical property data confirmed this unexpected trend as the copolymer made with BDA exhibited the weakest mechanical properties. These results were explained by the higher occurrence of primary cyclization reactions in the case of BDA.

Introduction

Multifunctional monomers, often known as cross-linkers, are usually employed in free-radical polymerization to produce polymer networks with applications in medicine, pharmaceuticals, paints, column packing, optics, polymer additives, ion-exchange resins, and rubbers. When used in emulsion polymerization, cross-linkers allow control of particle morphology and enhancement of the mechanical properties of latexes used for paints, coatings, impact modifiers, and polymeric additives for other polymeric matrixes. Because the end-use properties of these products are to a great extent due to the polymer microstructure, a fundamental understanding of the mechanisms governing the formation of the polymer chains is of paramount importance to improve product design and manufacture.

When multifunctional monomers are copolymerized in batch with other vinyl monomers, the kinetics and the polymer architecture are strongly influenced because of the presence of pendant double bonds in the polymer chain. These pendant double bonds are involved in the following reactions[1−5] (Figure 1): (i) primary cyclization (intramolecular cross-linking), occurring when a growing radical reacts with a pendant double bond of the same growing primary chain, creating loops or cycles, (ii) secondary cyclization (intramolecular cross-linking), occurring when the growing radical reacts with a pendant double bond of the same macromolecule but belonging to a different primary chain, (iii) cross-linking (intermolecular cross-linking), occurring when a growing radical reacts with a pendant double bond belonging to the other chain.

Secondary cyclization and cross-linking are considered to produce cross-linking points that are elastically active, whereas the loops formed by primary cyclization led to elastically inactive cross-linking points.[1,2]

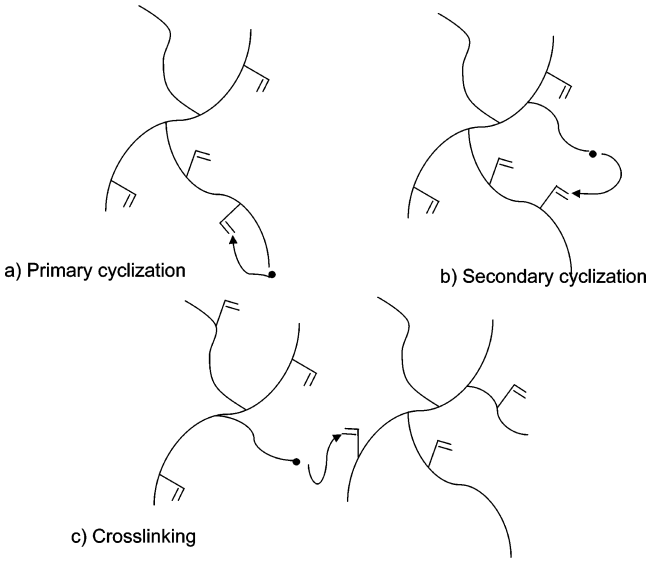

Figure 1. Reactions involving pendant double bonds.

An additional difference between emulsion polymerization and bulk and solution polymerization is that in emulsion polymerization the size of the gel is limited by the size of the polymer particle.

Dusek[2] and Matsumoto[6] reported that with some multifunctional monomers (diallyl compounds) and under certain reaction conditions the intramolecular cross-linking primary cyclization can take place within the same multifunctional monomer, which is also referred to as cyclopolymerization.

Most of the research studies reported in the literature with multifunctional monomers were carried out in batch conditions (bulk and solution polymerization) and with intermediate to high amounts of the multifunctional monomer (from a few percent to homopolymerization conditions) in the formulation.[2,3,5,6] The purpose of these investigations was the production of polymers for applications as superabsorbents (micro- and macrogels), as ionic exchange resins, in electronics, in lithog-

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† This paper is dedicated to Prof. Cecilia Sarasola.
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Table 1. Recipe and Properties of the Seed Latex Used in the Semibatch Experiments

	Formulation (g)		
butyl acrylate	350.5	$NaHCO_3$	1.75
water	900	$K_2S_2O_8$	1.77
SLS	7.0		
	Seed Properties		
intensity av particle size (nm)	97	gel fraction (wt %)	13
solids content (wt %)	28.8	level of branches (% C_q)	1.0

raphy, and others. The information generated in those works is of limited use in emulsion polymerization because in this process the polymer/monomer ratio (which strongly influences the reactions involving pendant double bonds) is much higher than in solution and bulk polymerization. In addition, the concentration of cross-linking agent used in emulsion polymerization is substantially lower than in bulk and solution polymerization.

Some works on the copolymerization of multifunctional monomer in emulsion polymerization have been reported. The batch emulsion polymerization of methyl methacrylate, MMA, with ethylene glycol dimethacrylate, EGDMA, is by far the system more often investigated.[7−12] Tobita et al.[7−9] compared experimental results with theoretical predictions,[13] finding that the average cross-linking density was high from the very beginning of the polymerization, contrary to what occurs in bulk or solution polymerization, and that the saturation monomer concentration in the particles decreases with increasing EGDMA concentration. To fit the experimental results, the reactivity of the pendant double bonds was considered to decrease as the cross-linker concentration increased. Tobita et al.[8] found that in the range 2.6−11.2 mol % EGDMA, the rate of polymerization was independent of the EGDMA concentration up to an intermediate conversion value. Beyond this value, the polymerization rate increased faster with larger contents of EGDMA. A limiting conversion, which decreased as the cross-linker content increased, was observed. Increasing the EGDMA content led also to higher average cross-linking densities. The difference with respect to bulk and solution polymerization was explained by the fact that, in the polymerization loci of emulsion polymerization, the swollen polymer particles, the concentration of polymer containing pendant double bonds, is higher than in the bulk from the beginning of the process. Tobita et al.[8,9,14] showed by Monte Carlo simulation that once the microgel is formed the molecular weight of the polymer increases linearly with conversion and that the MWD remains relatively narrow. In addition, they claimed that cross-linking reactions are predominantly intramolecular reactions (primary and secondary cyclization). The theoretical predictions were proven by using experimental data gathered by the group of Matsumoto for MMA/EGDMA and styrene/divinylbenzene[15] and for the homopolymerization of allyl methacrylate, AMA.[16] Guo et al.[11] have carried out an extensive kinetic study on the emulsion polymerization of MMA/EGDMA (EGDMA concentrations up to 25 wt %), finding that, for emulsifier concentrations above the cmc, the polymerization rate initially increased with the EGDMA concentration, but the polymerization rate at 25 wt % was lower than at 10 wt %. This is explained by two opposing effects of the increase of the cross-linking density: the decrease of the monomer concentration and the increase of the radical concentration in the polymer particles. Electron spin resonance (ESR) spectroscopy measurements showed a severe increase of the radical concentration in the last stages of the batch emulsion polymerization. Guo et al.[11] explained this result by considering that radicals get trapped within the cross-linked polymer network.

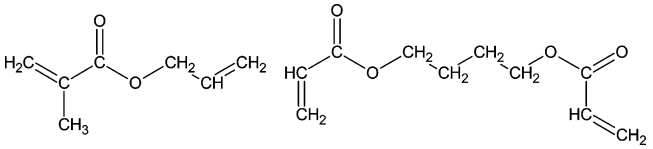

Figure 2. Chemical structures of AMA and BDA.

Matsumoto et al.[12,17,18] investigated the batch emulsion homopolymerization of AMA and the batch emulsion copolymerization of AMA with MMA, butyl methacrylate, BMA, propyl methacrylate, PMA, and EGDMA, as well as the copolymerizations of MMA with EGDMA and BMA with 1,6-hexanodiol dimethacrylate, HDDMA. Their results show that, in the presence of high concentrations of cross-linker (always higher than 5 mol %), the whole particle was gelled. For high T_g polymers (e.g., MMA) core−shell morphology may be developed.[18]

The emulsion copolymerizations discussed above were carried out in batch and using high concentrations of cross-linkers. However, commercial emulsion polymerization is commonly carried out in semicontinuous reactors in which the polymer/monomer ratio is much higher than in the batch process, and using relatively low concentrations of cross-linking agents. This difference affects both the kinetics and polymer architecture. Therefore, in the present work, the kinetics of the seeded semicontinuous emulsion copolymerization of BA with allyl methacrylate (AMA) and butanediol diacrylate (BDA), the effect of these cross-linkers in both microstructural properties (branching, cross-linking, gel content, and sol MWD), and the mechanical properties of the resulting polymer were investigated.

Experimental Section

Materials. Technical grade butyl acrylate (BA; Quimidroga S.A.), sodium lauryl sulfate (SLS; Merck), sodium hydrogen carbonate ($NaHCO_3$; Panreac), disodium hydrogen phosphate (Na_2HPO_4; Panreac), potassium persulfate (KPS; Fluka), AMA (Aldrich), and BDA (Atofina) were used as received. All polymerizations were carried out using doubly deionized water (DDI).

The chemical structure of the two cross-linkers is shown in Figure 2. 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 ratios of these double bonds with BA the methacrylic double bond is more reactive than the acrylic double bond, which is significantly more reactive than the allylic one.[12,17,19]

Polymerizations. All reactions were seeded. The poly(butyl acrylate) seed was prepared batchwise at 65 °C using the formulation of Table 1, which also shows the seed properties. The semicontinuous experiments were carried out at 80 °C with the formulation shown in Table 2 in a 1 L jacketed glass reactor agitated with a three-blade impeller at 200 rpm and using a feeding time of 3 h. Each cross-linker was used at two

Table 2. Recipe Used for the Seeded Semicontinuous Emulsion Copolymerizations of Butyl Acrylate with the Different Difunctional Cross-Linkers at 80 °C

	initial charge	stream 1	stream 2	total
seed polymer mass (g)	20.8			20.8
DDI water mass (g)	85[a]	410	23.25	518.25
SLS mass (g)	0.17	2.86		3.03
Na_2HPO_4 mass (g)		1.29		1.29
butyl acrylate mass (g)		234		234
cross-linker[b] (mol %)		0.23, 2.3		
$K_2S_2O_8$ mass (g)	0.155		0.55	0.705

[a] Included the water of the seed. [b] Mole percent based on the total monomer.

different concentrations, 0.23 and 2.3 mol % based on the total number of moles of BA as summarized in Table 3. Moreover, for comparison purposes, a reference experiment was performed without cross-linker, namely, a homopolymerization of BA. The experimental procedure was as follows: the seed and a fraction of water, SLS, and KPS were initially charged into the reactor. The rest was fed in two streams having the same feeding time. One of the streams was a pre-emulsion of the monomer mixture and the other an aqueous solution of the initiator.

Characterization. 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 cross-linking density). Branching density was measured by ^{13}C NMR using a Bruker DPX 300 apparatus with a BBO probe operating at 75.5 MHz. The branching density corresponded to the number of quaternary carbons from the BA units at 48−49 ppm. Additional details on the measurements of branching for poly(BA) can be found elsewhere.[20−22] In the case of the copolymerization of BA with AMA, additional quaternary carbons from the methacrylic unit of AMA can be found but without impact on the branching measurements as these methacrylic quaternary carbons are perfectly identified by their chemical shift at 44−45 ppm[19] as shown in Figure 3. The 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 the carrier fluid at 1 mL/min. Swelling experiments were carried out in methyl ethyl ketone, MEK, for 24 h at ambient temperature. The swelling of the copolymer samples was calculated as the ratio between the weight of the swollen gel polymer and the dry weight of the gel polymer.

Additional details on the measurements of the gel content and sol MWD can be found elswhere.[20,21] A Rheometrics ARES apparatus was used to determine the glass transition temperature, T_g, the storage modulus in the rubbery region, $G_n°$, and the molecular weight between entanglement, M_e, of films prepared from the final latexes. The films for the dynamic mechanical analysis, DMA, were prepared in a circular Teflon mold in which a given mass of latex was introduced. The films were then dried at ambient temperature for three weeks and finally dried at 40 °C in a ventilated oven overnight. To measure the storage modulus and the loss tangent as a function of temperature, time−temperature scans were performed with the DMA. A sinusoidal tensile force with a frequency of 1 Hz was applied to the sample while the temperature was raised 5 °C/min. Two geometries were used

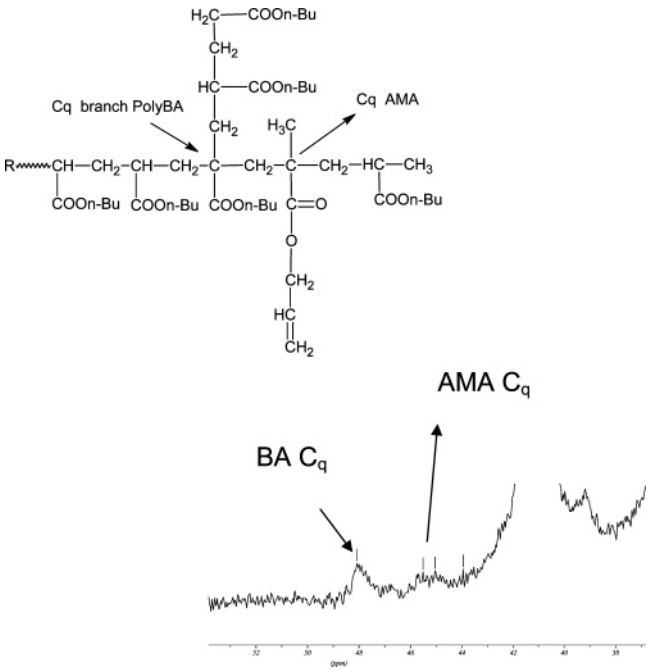

Figure 3. Quaternary carbon area of a ^{13}C NMR spectrum of the BA/AMA copolymer.

to cover the temperature range between −125 and +200 °C: (i) rectangular torsion from −125 to −10 °C (sample dimension of about 25 × 6 mm) and (ii) plate−plate geometry of diameter 10 mm from −50 to +200 °C.

Additional experiments using a melt elongational rheometer were performed to measure the deformation at constant elongation of 0.1 s^{-1} and ambient temperature (sample size 50 × 6 mm).

The storage modulus of the polymer in the rubbery region was used to calculate the molecular weight between cross-links, M_e, from the following equation:[23,24]

$$M_e = \rho RT/G_n^0$$

where ρ is the density of the copolymer, R is the gas constant, T is the absolute temperature, and $G_n°$ is the storage modulus in the rubbery region. This equation is valid provided that the material behaves as an ideal rubber produced in a homogeneous system, the chain end effects can be neglected (i.e., the kinetic chain length is much greater than the distance between cross-links), the chains between cross-links behave as Gaussian chains, and the storage modulus is much greater than the loss modulus.[23] Although the polymer films were formed from a cross-linked polymer latex, for the sake of comparison between the different systems, it was assumed that these conditions were fulfilled.

Results and Discussion

Figure 4 shows the instantaneous conversion for the polymerizations carried out without and with different concentrations of cross-linkers. After the initial stages of the process in which some monomer accumulation was observed, the process evolved under rather starved conditions (instantaneous conversion greater than 90%). Furthermore, the addition of either BDA or AMA did not significantly affect the kinetics, which is basically

Table 3. Summary of the Seeded Semicontinuous Emulsion Copolymerizations

run	cross-linker	cross-linker concn (mol %)	run	cross-linker	cross-linker concn (mol %)
SC 0		0	BA/BDA 1	BDA	0.23
BA/AMA 1	AMA	0.23	BA/BDA 2	BDA	2.3
BA/AMA 2	AMA	2.3			

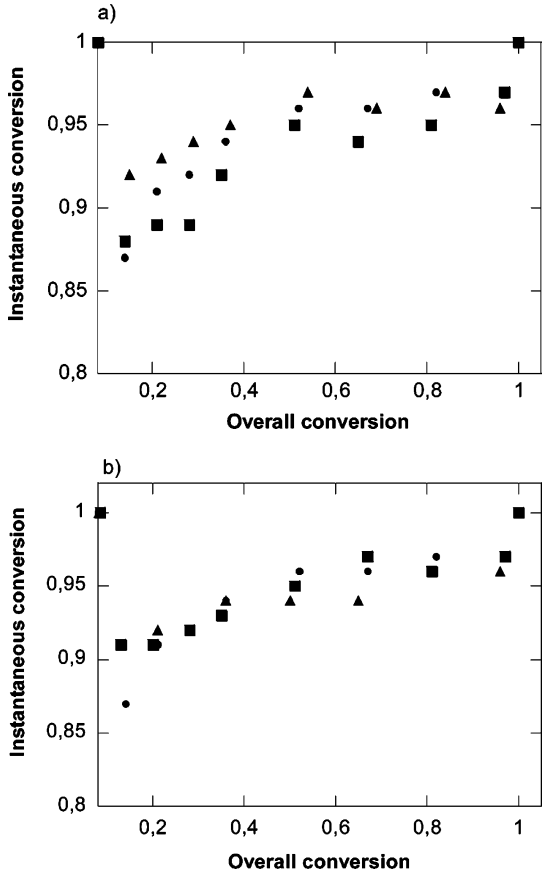

Figure 4. Effect of the cross-linker concentration on the kinetics of the seeded semicontinuous emulsion copolymerization of BA: (a) BDA and (b) AMA. Legend: (●) 0 mol %; (▲) 0.23 mol %; (■) 2.3 mol %.

controlled by the monomer feed rate. In addition, the growth of the particle size with conversion (not shown) was rather similar for all the polymerizations.

Figure 5 and Table 4 show the evolution of gel content for the experiments carried out with cross-linker and the final gel content for all experiments, respectively. It can be seen that the amount of gel was greater for the experiments carried out with cross-linker than for the homopolymerization of BA, and that the gel content increased with the concentration of cross-linker. In the homopolymerization of BA, gel was mainly formed by the intermolecular transfer to polymer followed by bimolecular termination by combination[20,21,25] (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). On the other hand, when the divinylic monomers were used, the cross-linking reaction (propagation to the pendant double bond of the divinylic monomer) was predominant (the amount of gel is double from the beginning of the process), and it was

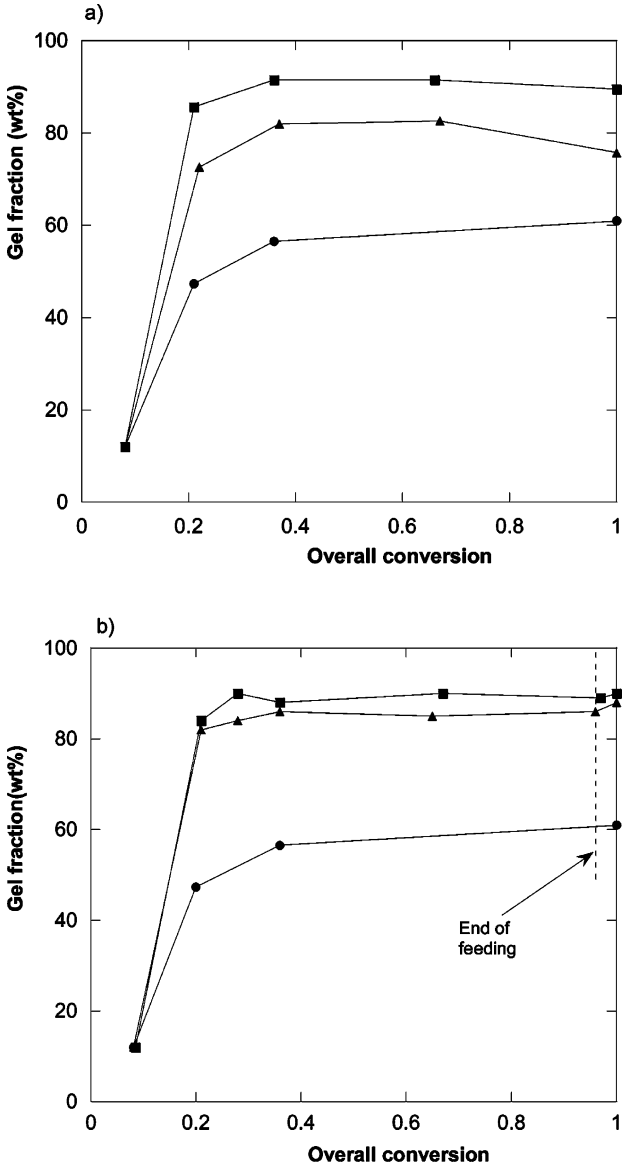

Figure 5. Evolution of the gel fraction for the seeded semicontinuous emulsion copolymerizations carried out with different concentrations of (a) BDA and (b) AMA. Legend: (●) 0 mol %; (▲) 0.23 mol %; (■) 2.3 mol %.

the main mechanism of gel formation and cross-linking (see Figure 6). Figure 5 shows that, in the experiments carried out with 0.23 mol % cross-linker, the gel fraction obtained with AMA was greater than that produced with BDA. This was not expected because of the higher reactivity of the pendant double bond of BDA (acrylic) as compared with that of AMA (allylic).[19]

On the other hand, in the experiments carried out with 2.3 mol % cross-linker, the evolution of gel content was rather similar for both cross-linkers.

Another important aspect that can be seen in Figure 5 is the evolution of the gel fraction in the late stages

Table 4. Final Gel Content, Level of Branching from Quaternary Carbons, Swelling Values (in MEK) and Sol Average Molecular Weight of the Latexes Produced in the Seeded Semicontinuous Copolymerizations of BA with Cross-Linkers

run	cross-linker (mol %)	gel (wt % in THF)	% C_q	swelling(w/w)	sol $\overline{M_w}$
SC 0	0	61 ± 1.83	2.2 ± 0.20	22.8 ± 1.60	40500
BA/BDA 1	0.23	76 ± 2.28	2.9 ± 0.26	16.5 ± 1.16	32800
BA/BDA 2	2.3	89 ± 2.67	3.7 ± 0.33	10.6 ± 0.74	15800
BA/AMA 1	0.23	88 ± 2.64	3.0 ± 0.27	11.5 ± 0.81	26400
BA/AMA 2	2.3	90 ± 2.70	5.4 ± 0.49	5.4 ± 0.38	6080

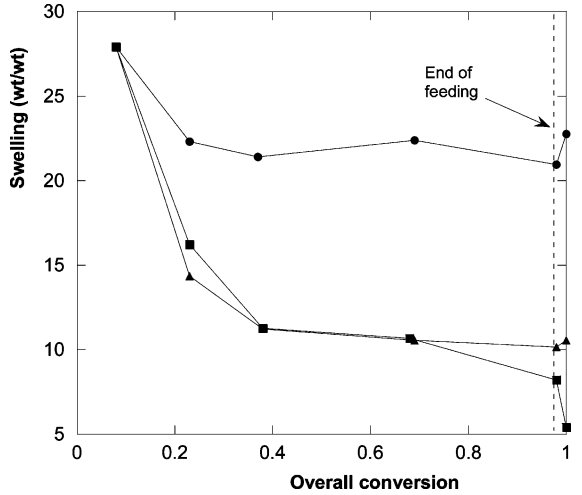

Figure 6. Evolution of the swelling for the seeded semicontinuous emulsion copolymerizations carried out with 2.3 mol % BDA and AMA. Legend: (●) BA; (▲) BA/BDA 2; (■) BA/AMA 2.

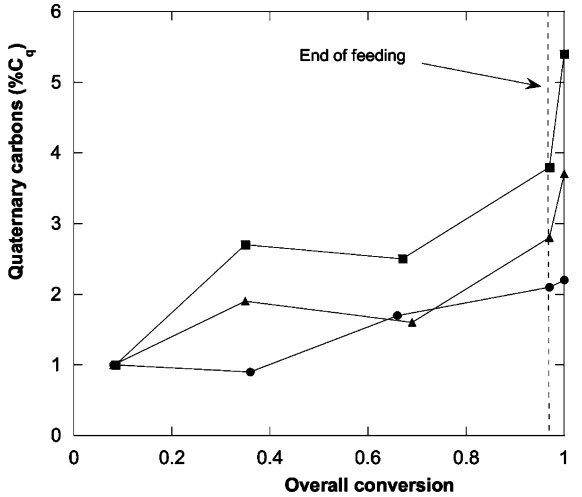

Figure 7. Evolution of % C_q for the seeded semicontinuous emulsion copolymerizations carried out with different cross-linkers at 2.3 mol %. Legend: (●) BA; (▲) BA/BDA 2; (■) BA/AMA 2.

of the process, namely, once the feeding of the monomers is completed. For the BDA and for both concentrations used, the gel slightly decreased in the last stages, whereas for AMA the gel increased, which is likely due to the late consumption of the pendant allylic double bonds due to its low reactivity.

Figure 6 and Table 4 display the evolution of the swelling of the gel fraction of the latexes obtained with 2.3 mol % cross-linker and the values for all the final latexes, respectively. The swelling value of a polymer is inversely proportional to the cross-linking density;[26] namely, the more cross-linked the polymer the less its swelling capability. Figure 6 and Table 4 show that the latexes prepared with BDA and AMA were more cross-linked (lower swelling value) than the homopolymer of BA. In addition, the final latexes produced with AMA were more cross-linked than the latexes with BDA for both cross-linker concentrations, which seems contradictory because of the higher reactivity of the pendant double bond of the BDA. A closer look at Figure 6 shows that the cross-linking density evolved in a different manner for both cross-linkers. Whereas at the beginning of the process (overall conversion ca. 20%) and during the plateau period (overall conversion up to 70%) the copolymer with BDA was more or equally cross-linked compared to that with AMA, at the end of the process the cross-linking density of the polymer containing AMA was greater. This trend was accelerated during the cooking period, in which the cross-linking density significantly increased for the copolymer produced with AMA, while for the BDA there was no additional change.

This evolution suggests that (a) BDA reacted faster, (b) there were AMA pendant double bonds (presumably allylic) available to participate in cross-linking reactions during cooking, (c) there were no BDA double bonds available during cooking, and (d) BDA used some double bonds in reactions that did not yield effective cross-linking. Points a−c can be explained by the higher reactivity of the pendant double bond of the BDA (acrylic vs allylic in the AMA). A possible explanation for point d is that primary cyclization[6,23,27,28] (intramolecular cross-linking reaction) was more important for BDA than for AMA. This intramolecular cross-linking reaction, as shown in Figure 1, forms cycles or loops which are not elastically efficient and hence do not contribute in the polymeric network. Therefore, the efficiency of the cross-linking density is reduced,[2,28,29] and the swelling increases. Interestingly, the evolution of swelling correlates well with the evolution of the gel in the late stages of the polymerization. Whereas for the polymerizations with BDA the gel fraction slightly decreases, for AMA the gel fraction increases, likely due to cross-linking reactions of the available pendant allylic double bonds.

NMR and FTIR spectroscopies were used to detect the presence of cycles or loops within the polymer chains. In none of the cases was evidence of the formation of cycles confirmed, likely because of the small amount of cycles formed and because cycles with more than five to six carbon atoms are extremely difficult to distinguish from linear configurations even in simple organic molecules.

Figure 7 presents the evolution of the percentage of quaternary carbons (% C_q) for the experiments carried out with 2.3 mol % AMA and BDA. Table 4 indicates the final % C_q for the experiments carried out without and with cross-linkers. It is worth explaining that the quaternary carbons (measured from the spectra at 48−49 ppm[20,21]) were formed by intramolecular (backbiting) and intermolecular chain transfer to the polymer. In the homopolymerization of BA, most of the branches are short branches formed by backbiting and the level of branching and gel content are not directly correlated because the gel is formed by intermolecular chain transfer to the polymer followed by termination by combination.[20,21,31,32] The copolymerizations of BA with BDA and AMA do not yield either quaternary carbons or new sites prone to suffering H abstraction that upon propagation will lead to a quaternary branch point. As explained in the Experimental Section, AMA contains a quaternary carbon in the methacrylic group, see Figure 3, but the chemical shift of this group at 44−45 ppm[19] is different from that of the quaternary carbons formed by the chain transfer to polymer. Note also that the cross-link points produced with these cross-linkers do not form quaternary carbons.

Figure 7 presents some interesting features. First, the fraction of quaternary carbons in the experiments with cross-linker was higher than in the absence of cross-

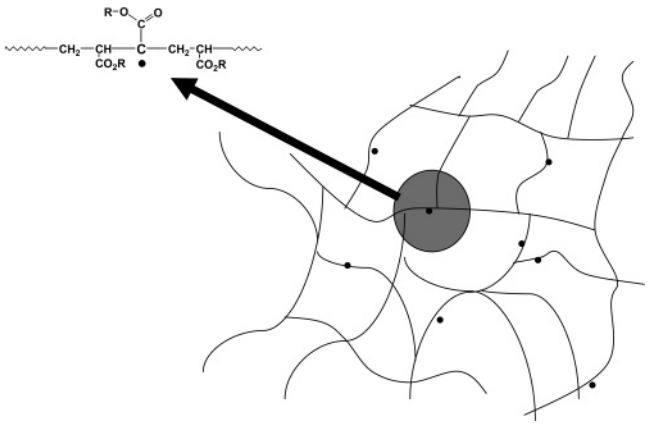

Figure 8. Structure of trapped acrylate radicals.

linker, even though the copolymerization of the cross-linker does not directly produce more branching. Second, an important increase of % C_q during the cooking period was observed: in approximately 3% monomer conversion, % C_q increased from 2.7% to 3.8% for BDA and from 3.9% to 5.3% when AMA was used. Plessis et al.[20,21,31,32] reported that backbiting was the predominant branching mechanism (quaternary carbon formation) in the polymerization of BA. Likely, backbiting was also the predominant mechanism for quaternary carbon formation during these copolymerizations. However, the amount of monomer remaining, during the cooking period, was not enough to justify the strong increase in % C_q, and hence, other mechanisms should be responsible for the additional C_q formation. Third, in the experiments using 2.3% cross-linker, % C_q was higher for AMA than for BDA and the increase during the cooking was also more important for AMA. Table 4 shows that, in the experiments carried out using a lower concentration of cross-linker (0.23 mol %), the % C_q values obtained with both cross-linkers were similar (2.9% and 3% for BDA and AMA, respectively), but still higher than for the homopolymerization of BA.

A mechanism that may justify these results is as follows: Radicals entering into the polymer particles will grow slowly because of the low monomer concentration (it is worth pointing out that swelling a highly cross-linked polymer is difficult, and hence, the monomer partitioning is shifted toward the aqueous phase as compared with that of a non-cross-linked system).[7,9] On the other hand, the polymer concentration is very high, and hence, it is likely that the growing radical suffers intermolecular chain transfer to polymer. These situations are likely favored in densely cross-linked polymers, namely, at a high concentration of cross-linkers or in the case of cross-linkers leading to highly dense networks as in the case of AMA. Also low monomer concentrations will favor this situation as it occurred during the cooking period. Because the probability of receiving the transferred radical is higher for large macromolecules, most likely an intramolecular chain transfer to the gel will occur. The tertiary radical formed in the gel (Figure 8) is significantly less reactive than the secondary BA radicals entering into the polymer particles, and in addition, the monomer concentration is very low. This will lead to an accumulation of tertiary radicals in the gel (trapped radicals in the gel have been detected by ESR[11]). Some of these radicals may in due course react with the monomer, producing quaternary carbons, which are detected by ^{13}C NMR.

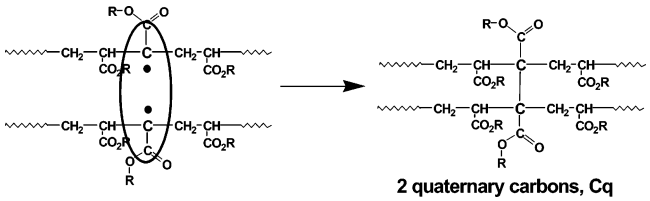

Figure 9. Structure resulting from the termination by combination of two trapped acrylate radicals.

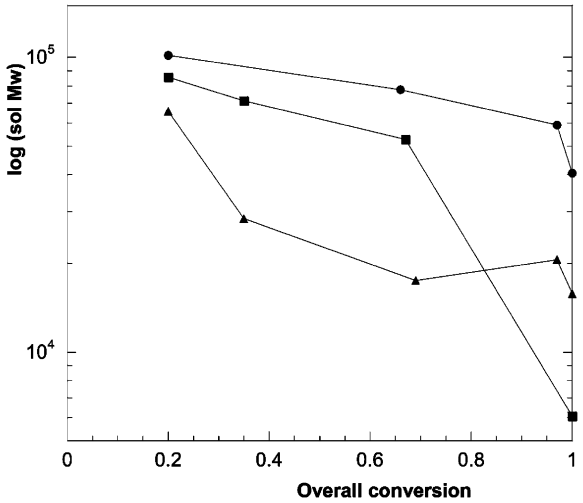

Figure 10. Evolution of the sol weight-average molecular weight for the seeded semicontinuous emulsion copolymerizations carried out with 2.3 mol % AMA and BDA. Legend: (●) BA; (▲) BA/BDA 2; (■) BA/AMA 2.

The tertiary radicals may also suffer termination by combination, giving two quaternary carbons (Figure 9). It is unlikely that the tertiary radicals trapped in the network have a significant diffusion rate. Nevertheless, diffusion is not the only way through which radicals can move, because hydrogen transfer introduces a mobility of the radical sites in the polymer.[3,33−38]

Figure 10 presents the sol weight-average molecular weights ($\overline{M}_w$) of samples taken during the seeded semicontinuous experiments with (2.3 mol %) and without cross-linker. Table 4 shows the final values of the sol $\overline{M}_w$ for the reactions with and without cross-linker. The sol polymer injected into the GPC apparatus was that recovered from the swelling experiments. It can be seen that the molecular weight decreased during the reaction. Interestingly, the sol $\overline{M}_w$ of the BA/AMA copolymer was initially higher than that of the BA/BDA copolymer (in agreement with the lower cross-linking density) of the BA/AMA system, Figure 6, but at the end of the process, the sol molecular weight for the BA/AMA copolymer was lower than that prepared with BA/BDA. The same trend was also observed for the emulsion copolymerizations carried out with a concentration of cross-linker of 0.23 mol%. It is also noticeable that the sol molecular weight for the BA homopolymer was larger than those of the polymers containing cross-linkers. The reason is that long chains are predominantly incorporated into the gel, yielding a lower sol MW.

DMA was performed to measure the glass transition temperature, T_g, the storage modulus, $G_n°$, and molecular weight between cross-links, M_e. In addition, a melt elongational rheometer, MER, was used to measure the strength at constant elongation at which the sample

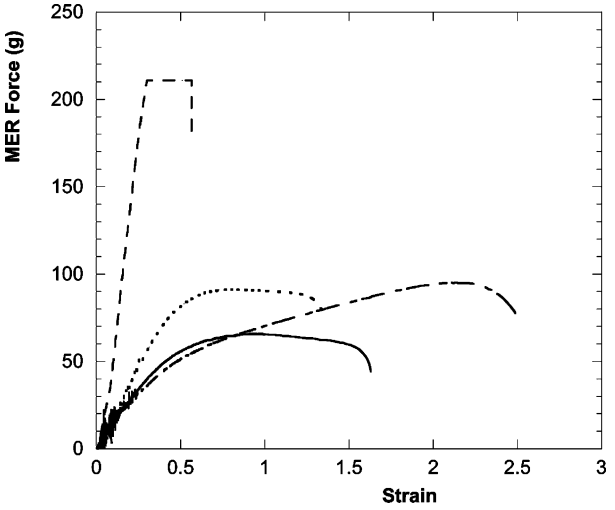

Figure 11. Evolution of the MER force for the polymer films obtained in the semicontinuous emulsion copolymerizations of BA with cross-linkers. Legend: (---) BA/BDA 1; (– – –) BA/BDA 2; (—) BA/AMA 1; (- – -) BA/AMA 2.

Table 5. Results of DMA and MER Measurements for the Final Latexes Produced in the Semicontinuous Experiments Carried out with BDA and AMA

run	T_g (°C)	$G_n°$	M_e	MER strength
BA/BDA 1	−34.2	1.27×10^5	18874	32.2
BA/BDA 2	−34	1.34×10^5	17837	47.9
BA/AMA 1	−34.9	1.40×10^5	17209	29.4
BA/AMA 2	−31.1	5.95×10^5	4039	200

breaks. In this case, the higher the strength measured, the higher the cross-linking density. Table 5 shows the results obtained in the experiments carried out without and with cross-linkers. For the experiments carried out with 0.23 mol % cross-linker, the results of T_g, $G_n°$, M_e, and the MER strength are quite similar, in agreement with the similarities shown in the structural properties. In the experiments with 2.3 mol %, the T_g and the storage modulus of the copolymer with AMA were higher than those obtained with BDA. The M_e obtained with AMA is approximately one-fourth of that with BDA. The MER strength was 4 times higher for the AMA copolymer than for the BDA one. Thus, it can be concluded that, at 2.3 mol % cross-linker, the BA/AMA copolymer was about 4 times more densely cross-linked than the BA/BDA one, which is consistent with what was observed in the branching and swelling data, and it is in agreement with data reported by Elliot et al.[23] These authors copolymerized 2-methoxyethyl methacrylate with different isomers of cyclohexanediol dimethacrylate (1,4-CHDDMA, 1,3-CHDDMA, and 1,2-CHDDMA). Free-radical copolymerization of these systems at different cross-linker concentrations showed that autoacceleration occurred at lower conversions with 1,4-CHDDMA than with 1,2-CHDDMA. The DMA analysis of the polymer films showed that the T_g was higher and the M_e lower for copolymers with 1,4-CHDDMA. Elliot et al.[23] explained these results in terms of the higher cyclization rate of the 1,2-CHDDMA, which formed a less cross-linked network (more cyclized network). In this less cross-linked network, the mobility of the polymer chains is less affected and the termination rate decreased slower, delaying the onset of autoacceleration.

Figure 11 shows the curves of the MER experiments carried out for the copolymers produced in the seeded semicontinuous copolymerizations of BA with cross-linkers. It can be seen that the higher the amount of cross-linker, the higher the MER force, resulting from the more cross-linked polymer networks. At the higher concentration of cross-linker, the MER force was about 4 times higher for the AMA polymer film than for the BDA one.

Conclusions

The effect of two cross-linkers (AMA and BDA) on the kinetics and the microstructural and mechanical properties of the polymers produced during the seeded semicontinuous emulsion polymerization of BA was studied. The results showed that the addition of the cross-linkers did not significantly affect the kinetics. On the other hand, branching, cross-linking, and sol molecular weights were strongly affected by the choice of the cross-linker. Surprisingly, the most reactive cross-linker (BDA) produced the less cross-linked latex. When AMA was used, the evolution of the cross-linking density demonstrated that it was during the cooking period when the unreacted allyl double bonds cross-linked and formed a highly cross-linked polymer. Furthermore, the % C_q and the gel content were higher for the experiments carried out with AMA; this can be explained by the fact that intramolecular chain transfer to the polymer is favored by the low monomer concentrations (achieved in the cooking period) and by the cross-linking density. The more dense the polymer network, the more likely intramolecular chain transfer to the polymer within the gel molecule will occur. Primary cyclizations were considered to be responsible for the lower cross-linking density obtained with BDA because these reactions lead to a loss of pendant double bonds in cycles, which are not elastically effective. However, no direct experimental proof of the presence of cycles on the network structure was obtained. Nevertheless, such a hypothesis was further confirmed with the results of the mechanical properties as the polymer films of latexes produced with AMA present significantly higher storage modulus and T_g values than those produced with BDA.

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References and Notes

(1) Tobita, H.; Hamielec, A. E. In *Polymer Reaction Engineering*; Reichert, K. H., Geisseler, W., Eds.; VCH Publishers: New York, 1989; p 43.
(2) Dusek, K. In *Network Formation Involving Polyfunctional Polymer Chains in Polymer Networks*; Stepto, R., Ed.; Blackie: London, Chapter 3, p 64.
(3) Kloosterboer, J. G. Network Formation by Chain Cross-linking Photopolymerization and its Application in Electronics. *Adv. Polym. Sci.* **1998**, *84*, 1.
(4) Elliot, J. E.; Bowman, C. N. *Macromolecules* **1999**, *32*, 8621.
(5) Dusek, K. Network Formation by Chain Cross-linking Copolymerization. *Dev. Polym.* **1982**, *3*, 143.
(6) Matsumoto, A. Free-radical Cross-linking Polymerization and Copolymerization of Multivinyl Compounds. *Adv. Polym. Sci.* **1995**, *123*, 41.
(7) Tobita, H.; Kimura, A.; Fujita, K.; Nomura, M. *Polymer* **1993**, *34*, 2569.
(8) Tobita, H.; Uemura, Y. *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 1415.
(9) Tobita, H.; Yoshihara, Y. *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 1415.
(10) Tobita, H.; Kumagai, M.; Aoyagi, N. *Polymer* **2000**, *41*, 481.
(11) Guo, H.; Hamielec, A. E.; Zhu, S. *J. Polym. Sci.* **1997**, *66*, 935.
(12) Matsumoto, A.; Otaka, T.; Aota, H. *Macromol. Rapid Commun.* **2001**, *22*, 607.

(13) Tobita, H.; Hamielec, A. E. *Macromolecules* **1992**, *25*, 2671.
(14) Tobita, H.; Yamamoto, K. *Macromolecules* **1994**, *27*, 3389.
(15) Nakamura, K.; Imoto, A.; Aota, H.; Matsumoto, A. In *Preprints for the 8th Polymeric Microsphere Symposium*, Nov 9−11, 1994, Fukui, Japan; p 37.
(16) Matsumoto, A.; Mori, Y.; Takahashi, S.; Aota, H. *Netsukokasei-Jushi* **1995**, *16*, 131.
(17) Matsumoto, A.; Kodama, K.; Mori, Y.; Aota, H. J. M. S. *Pure Appl. Chem*. **1998**, *A35*, 1459.
(18) Matsumoto, A.; Kodama, K.; Aota, H.; Capek, I. *Eur. Polym. J*. **1999**, *35*, 1509.
(19) Elliot, J.; Nie, J.; Bowman, C. N. *Polymer* **2003**, *44*, 327.
(20) Plessis, C. Modeling the molecular weight distribution of polyacrylic latexes in seeded semicontinuous polymerisation. Ph.D. Thesis, The University of the Basque Country, Donostia-San Sebastián, Spain, 2000.
(21) Plessis, C.; Arzamendi, G.; Leiza, J. R.; Schoonbrood, H.; Charmot, D.; Asua, J. M. *Macromolecules* **2000**, *33*, 5041.
(22) Ahmed, N. M.; Heathly, F.; Lovell, P. A. *Macromolecules* **1998**, *31*, 2822.
(23) Kannurpatti, A. R.; Anseth, J. W.; Bowman, C. N. *Polymer* **1998**, *12*, 2507.
(24) Heatly, F.; Lovell, P. A.; McDonald, J. *Eur. Polym. J*. **1993**, *29*, 255.
(25) Plessis, C.; Arzamendi, G.; Leiza, J. R.; Schoonbrood, H.; Charmot, D.; Asua, J. M. *Ind. Eng. Chem. Res*. **2001**, *40*, 3883.
(26) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; p 587.
(27) Bouvier-Fontes, L.; Pirri, R.; Arzamendi, G.; Asua, J. M.; Leiza, J. R. *Macromol. Symp.* **2004**, *206*, 149
(28) Charmot, D. In *Polymeric Dispersions: Principles and Applications*; Asua, J. M., Ed.; Kluwer: Dordrecht, The Netherlands, 1997; p 79.
(29) Elliot, J.; Bowman, C. N. In *Wiley Polymer Networks Group Review Series*; Stokke, B. T., Elgasaeter, A., Eds.; John Wiley and Sons: New York, 1999; Vol. 2, p 27.
(30) Charmot, D.; Guillot, J. *Polymer* **1992**, *33*, 352.
(31) Plessis, C.; Arzamendi, G.; Alberdi, J. M.; Van Herk, A. M.; Leiza, J. R.; Asua, J. M. *Macromol. Rapid Commun*. **2003**, *24*, 173.
(32) Arzamendi, G.; Plessis, C.; Leiza, J. R.; Asua, J. M. *Macromol. Theory Simul*. **2003**, *12*, 315.
(33) Kloosterboer, J. G.; Lijten, G. F. C. M. *Polym. Commun*. **1987**, *28*, 2.
(34) Ranby, B.; Rabek, J. F. *ESR Spectroscopy in Polymer Research*; Springer: Berlin, 1977.
(35) Szocs, F.; Lazar, M. *Eur. Polym. J. (Suppl.)* **1969**, 137.
(36) Wen, M.; McCormick, A. V. *Macromolecules* **2000**, *33*, 9247.
(37) Wen, M.; Scriven, L. E.; McCormick, A. V. *Macromolecules* **2003**, *36*, 4140.
(38) Wen, M.; Scriven, L. E.; McCormick, A. V. *Macromolecules* **2003**, *36*, 4151.

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