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# Effect of the Diacrylate Ester Size on the Semicontinuous Cross-Linking Emulsion Copolymerization of BA

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ABSTRACT: The seeded semicontinuous emulsion copolymerization of butyl acrylate (BA) with a series of diacrylate cross-linkers at 80 °C and using potassium persulfate as initiator was investigated. The influence of the diacrylate ester size on the kinetics, branching and cross-linking density, molecular weight between entanglements, gel fraction, sol molecular weight, and mechanical properties (glass transition temperature and storage modulus) was investigated. It was found that the shorter the diacrylate, the less cross-linked the polymer and the lower the glass transition temperature and the storage modulus. This effect was explained by a higher cyclization rate of the shorter diacrylates due to energetically favored cycle formation.

## Introduction

Polymer latices obtained by emulsion polymerization find applications in the manufacture of adhesives, coatings, synthetic rubbers, thermoplastics, and biomedical technology. The application of these products is mainly dominated by the polymer properties, which in turn depends on the polymer microstructure. In many industrial important cases, the polymer microstructure is modified by using multifunctional monomers, often known as cross-linkers.

Despite the practical importance of these systems, the works reporting in the open literature about the kinetics and the mechanisms involved in the formation of the microstructure of the polymers produced in the emulsion copolymerization of vinylic monomers with multifunctional monomers are scarce. In addition, most of the works were carried out in batch reactors, which yield polymer microstructures rather different from those obtained in semicontinuous systems used in practice. Furthermore, the amount of cross-linker employed exceeds that used in commercial practice.[1−11] Several works reported the homo- and copolymerization of diacrylates and dimethacrylates with monovinylic monomers, but most of them were made in bulk polymerization.[12−34] Even though the monomer/polymer ratio and the mechanism for radical initiation (which to a large extent determine the polymer microstructure formation) of the bulk process are different from those of the semicontinuous emulsion polymerization, valuable information can be obtained from bulk polymerization.

Thus, the distinctive mechanisms that occur during the polymerization of vinyl monomers with multifunctional monomers are well established.[15−18,20−22,34] Basically three additional reactions have been identified as responsible for the changes that occur in both kinetics and microstructure of the polymer: (i) primary cyclization (intramolecular cross-linking) which is the reaction of a growing radical with a pendant double bond of the same growing chain creating loops or cycles within the network; (ii) secondary cyclization (intramolecular cross-linking), that is the reaction of the growing radical with a pendant double bond of the same chain but not belonging to the same growing primary chain; and (iii) cross-linking (intermolecular cross-linking), which is the reaction of a growing radical with a pendant double bond belonging to other chain. The latter two cross-linking reactions 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.

The group of Bowman[19,20,23,25,26] has studied the network formation during the bulk copolymerization of multi(meth)acrylates and particularly the influence of the distance between the double bonds of the monomer on the onset of gelation and the occurrence of primary cyclization reactions as well as on the mechanical properties of the polymers. In agreement with the observations of Matsumoto et al.[29] for the homopolymerizations of dimethacrylates of different ester sizes, Bowman et al.[25,26] found that the longer the separation of the functional groups, the earlier was the onset of autoacceleration in the copolymerization with small amounts of cross-linker ($<10\%$). Furthermore, the copolymers made with cross-linkers having larger separation between the functional groups exhibited a lower molecular weight between cross-link points and a higher glass transition temperature ($T_g$) than the analogous cross-linker with shorter distance between the functional groups. This was attributed to a predominant cyclization over cross-linking reactions for the case of shorter analogues, which allowed some mobility of the polymer chains and hence delayed the onset of gelation.

Mathematical models[8−10,21−24,35,36] have been developed to explain network formation in cross-linking polymerization considering the importance of primary and secondary cyclization and cross-linking. Statistical models,[16] Monte Carlo simulations,[8−10] kinetic

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**Table 1. Formulation and Seed Properties**

| formulation | |
|---|---|
| butyl acrylate (g) | 350.5 |
| water (g) | 900 |
| SLS (g) | 7.0 |
| $NaHCO_3$ (g) | 1.75 |
| $K_2S_2O_8$ (g) | 1.77 |
| seed properties | |
| intensity average particle size[a] (nm) | 97 |
| solids content (wt %) | 28.8 |
| gel fraction[b] (wt %) | 13 |
| level of branches[c] (% $C_q$) | 1.0 |

[a] Dynamic light scattering (N4 Coulter). [b] Extraction in THF at reflux (75 °C). [c] $^{13}C$ NMR (Bruker DPX 300).

**Table 2. Recipe Used for the Seeded Semicontinuous Emulsion Copolymerization of BA/Diacrylates**

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

[a] Based on monomers.

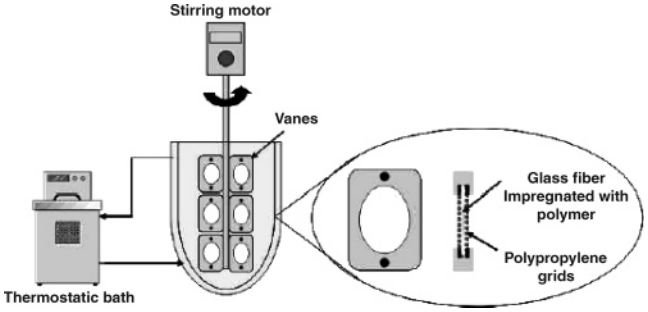

**Figure 1.** Experimental setup designed for gel fraction measurement.

models,[21−24] and kinetic gelation models[35,36] have been used to describe the complex kinetic and reactivities of the pendant double bonds under reaction conditions.

In a previous paper,[37] the effect of the cross-linker reactivity on the copolymer microstructure in the semicontinuous emulsion copolymerization of BA with butanediol diacrylate (BDA) and allyl methacrylate (AMA) was investigated. Unexpectedly, the less reactive cross-linker, AMA, produced the copolymers that were more cross-linked and more branched (in terms of quaternary carbons) than those obtained with BDA. This feature was explained by a higher cyclization efficiency of BDA than AMA that consumed the pendant double bonds in intramolecular cross-linking reactions (primary cyclization) yielding cycles or loops that do not contribute efficiently in the cross-linking density. In this work a series of diacrylates of different ester size were used as cross-linker in the seeded semibatch emulsion copolymerization of BA and the kinetics, microstructure, and mechanical properties of the resulting copolymers investigated. The cross-linkers used were the ethylene glycol diacrylate, EGDA, the butanediol diacrylate, BDA, the 1,6-hexanediol diacrylate, HDDA, and the poly(ethylene glycol) diacrylate, PEGDA.

## Experimental Section

**Materials.** 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 ($K_2S_2O_8$, Fluka), ethylene glycol diacrylate (Aldrich), butanediol diacrylate (Atofina) 1,6-hexanediol diacrylate (Cray Valley), and poly(ethylene glycol) diacrylate (Cray Valley) were used as received. All polymerizations were carried out using deionized water (DDI).

**Polymerizations.** All reactions were seeded. The poly(butyl acrylate) seed was prepared batchwise at 65 °C using the formulation of Table 1. This table also shows the properties of the seed. The semicontinuous experiments were carried out at 80 °C with the formulation shown in Table 2 in a 1 L jacketed reactor agitated with a three-blade impeller at 200 rpm and using a feeding time of 3 h. Each cross-linker was used at a concentration of 2.3 mol % based on the total number of moles of BA. Moreover, for comparison purposes, a reference experiment was performed without cross-linker, namely, a homopolymerization of BA. In the semicontinuous experiments, the seed, and a fraction of water, SLS and KPS were initially charged into the reactor. Then a preemulsion of the monomer/cross-linker mixture and an initiator solution were fed for 3 h.

**Characterization.** During the polymerization, samples were withdrawn from the reactor at regular sampling times and analyzed to measure the monomer conversion, the percentage of quaternary carbons (% Cq), the gel content, the sol MWD, and the swelling (which gives an indirect indication of the cross-linking density). Monomer conversion was determined by gravimetry. In the copolymerization of BA with diacrylates, branching points result from intermolecular and intramolecular chain transfer to polymer and from the diacrylates. The branching points produced by chain transfer to polymer are quaternary carbons that were 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 a continuous extraction with THF under reflux conditions in a 2 L glass reactor at 75 °C for 8 h. Figure 1 shows the experimental setup designed for the gel measurement. A glass fiber mat was impregnated with a few droplets of latex and dried overnight in an oven at 50 °C. The mat was placed in a vane and is immersed in the THF while stirred for 8 h, as shown in Figure 1. Up to eight stainless steel vanes can be fixed to the shaft, making possible to measure several samples at the same time under the same conditions.

Sol MWD was measured from samples obtained from the sol fraction of the swelling experiments (see below) 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) for 24 h at ambient temperature. Swelling was calculated as the ratio between the weight of the swollen gel polymer and the weight of the gel polymer. A Rheometrics ARES apparatus was used to perform the dynamic mechanical analysis (DMA) of films prepared with the final copolymers. These measurements allowed to determine the glass transition temperature, $T_g$, and the storage modulus in the rubbery region, $G_n°$. The molecular weight between entanglements, $M_e$, was calculated from $G_n°$. The DMA films were cast from latex in a circular Teflon mold. The films were then dried at ambient temperature for 3 weeks and finally dried overnight at 40 °C in a ventilated oven. Time−temperature scans were carried out to measure the storage modulus and the loss tangent as a function of temperature. A sinusoidal tensile force with a frequency of 1 Hz was applied to the sample while raising the temperature 5 °C/min. Two geometries were used to cover the temperature range between −125 and 200 °C: rectangular torsion from −125 up to −10 °C (sample dimensions of about 25 × 6 mm); plate−plate of a diameter of 10 mm from −50 to 200 °C.

The storage modulus of the polymer in the rubbery region was used to calculate the molecular weight between entangle-

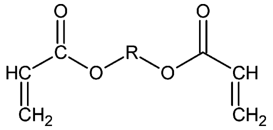

**Figure 2.** Chemical structure of ethylene glycol diacrylate (EGDA, R = 2 carbons), butanediol diacrylate (BDA, R = 4 carbons), 1,6-hexanediol diacrylate (HDDA, R = 6 carbons), and poly(ethylene glycol diacrylate) (PEGDA, R = 12 carbons).

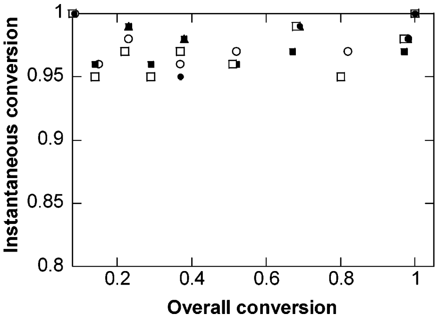

**Figure 3.** Effect of the diacrylate cross-linker length on the kinetics of the seeded semicontinuous emulsion copolymerizations of BA/diacrylate. Legend: (●) BA, (○) BA/EGDA, (▲) BA/BDA, (■) BA/HDDA, and (□) BA/PEGDA.

ments, $M_e$, using the following equation:[25,26]

$$M_e = \frac{\rho R T}{G_n{}^\circ} \tag{1}$$

where $\rho$ is the density of the copolymer, $R$ is the gas constant, $T$ is the absolute temperature, and $G_n{}^\circ$ is the storage modulus in the rubbery region. This equation is valid assuming the material behaves as an ideal rubber produced in a homogeneous system, chain ends can be neglected (i.e., the kinetic chain length is much greater than the distance between cross-links), chains between cross-links behave as Gaussian chains, and the storage modulus is much greater than the loss modulus. These conditions are usually met when the amount of cross-linker used is modest.

The cross-linkers are symmetrical divinyl monomers with two acrylate double bonds having the general structure shown in Figure 2. The length between the two acrylate double bonds was thus varied from 2 carbons (EGDA) to 12 carbons (PEGDA).

## Results and Discussion

Figure 3 shows the instantaneous conversion for the seeded semicontinuous emulsion copolymerization carried out without and with the different diacrylates. All the polymerizations evolved under rather starved conditions (namely, the instantaneous conversion was greater than 90%), and the ester size of the cross-linker did not significantly affect the kinetics. This differs from what was reported for batch bulk copolymerizations of dimethacrylates of different ester sizes[31] or isomeric cross-linkers[26] where the longer the cross-linker or the higher the distance between (meth)acrylate double bonds, the earlier the onset of the autoacceleration. However, under the conditions of this work, semicontinuous operation and starved conditions, the polymerization rate was basically controlled by the feeding rate that was the same in all runs.

Figure 4 shows the effect of the diacrylate cross-linker chain length on the evolution of the fraction of gel, and Table 3 gives the final gel content for all these experiments. It can be seen that the evolution of the gel content within the diacrylates was rather similar, namely, no effect of the ester size of the diacrylate was observed. In addition, the fraction of gel for the experiments carried out with cross-linker was much greater than for the homopolymerization of BA. Note that in the homopolymerization of BA gel was mainly formed by the intermolecular chain transfer to polymer plus the bimolecular termination by combination[38−40] (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 cross-linking reaction (propagation to the pendant double bond of the divinylic monomer) was predominant, and the gel was mainly due to cross-linking. As the experiments were carried out with diacrylates having the same type of vinyl double bond, the evolution of gel content is expected to be rather similar for the different cross-linkers, which is confirmed with the experimental results. Following the experimental results of Elliot and Bowman[25,26] which were modeled by these authors[22,23] and McCormick et al.,[35,36] it can be expected that with the long diacrylates the pendant double bonds lost in cyclization reactions would be lower, and hence more cross-linked copolymers would be obtained. This would suggest that the gel fraction should be higher as the size of the cross-linker was increased. However, as shown in the embedded plot in Figure 4, the only clear difference in gel formation is observed for EGDA, which yields the lower amount, as it would be expected for a larger waste of pendant double bonds by cyclization reactions. The nonsignificant difference found for the other diacrylates might be related to the low sensitivity of the extraction process employed to characterize gel content, particularly when the amount of gel polymer is relatively large (>80%) in the copolymer. Note that the amount of gel as measured in this work represents the insoluble

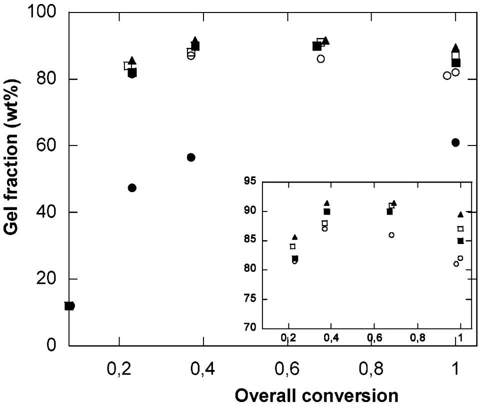

**Figure 4.** Evolution of the gel fraction for the seeded semicontinuous emulsion copolymerizations carried out with different diacrylates at 2.3 mol %. Legend: (●) BA, (○) BA/EGDA, (▲) BA/BDA, (■) BA/HDDA, and (□) BA/PEGDA.

**Table 3. Final Fraction of Gel (in THF), Level of Branching, Swelling Values (in MEK), and Sol Average Molecular Weight of the Latexes Produced in the Seeded Semicontinuous Copolymerizations of BA with Diacrylates**

| run | gel (wt % in THF) | quaternary carbons (%Cq) | swelling | sol $\overline{M}_w$ |
|---|---|---|---|---|
| BA | 61 ± 1.83 | 2.2 ± 0.20 | 22.8 ± 1.60 | 40 500 |
| BA/EGDA | 82 ± 2.46 | 4.1 ± 0.37 | 10.3 ± 0.72 | 26 500 |
| BA/BDA | 90 ± 2.70 | 3.7 ± 0.33 | 10.6 ± 0.74 | 15 800 |
| BA/HDDA | 85 ± 2.55 | 3.9 ± 0.35 | 8.9 ± 0.63 | 20 900 |
| BA/PEGDA | 87 ± 2.61 | 3.2 ± 0.29 | 8.8 ± 0.62 | 21 000 |

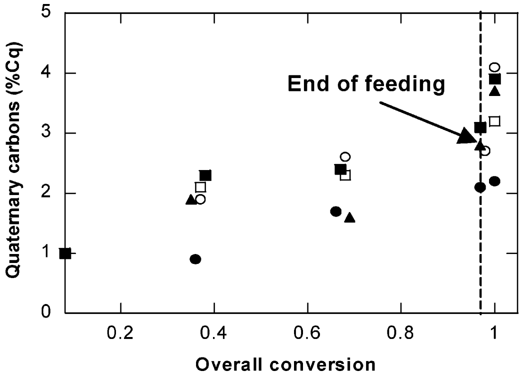

**Figure 5.** Evolution of the level of % Cq for the seeded semicontinuous emulsion copolymerizations carried out with different diacrylates at 2.3 mol %. Legend: (●) BA, (○) BA/EGDA, (▲) BA/BDA, (■) BA/HDDA, and (□) BA/PEGDA.

fraction of polymer in THF, and above a certain cross-linking density this process becomes not sensitive enough as to show differences. It is also worth noting that the amount of polymer in the seed employed in these experiments was less than 10 wt %. Furthermore, we found that the initial gel content of the seed had no effect on the final gel content produced during semibatch polymerizations.[38] A better insight into the effect of the size of the diacrylates on the microstructure (cross-linking density) should be obtained from other measurements, as is shown below.

Figure 5 presents the evolution of the quaternary carbons for the experiments carried out with the diacrylates, and Table 3 indicates also the final values of % Cq for the different experiments. For the sake of comparison, Figure 5 also includes the evolution of the branching measured in the absence of the cross-linking monomers. It is worth pointing out that quaternary carbons are only formed by intermolecular and/or intramolecular (backbiting) chain transfer to polymer (in the homopolymerization of BA most of the branches are short branches formed by backbiting[39−41]) and that copolymerization of the diacrylates does not yield either new branching (Cq) points or new sites prone to suffering H abstraction that upon propagation will lead to a quaternary branch point. Here we are assuming that the distribution of monomer is rather uniform in the polymer particles as supported by the good model predictions obtained in the emulsion polymerization of BA under similar semibatch conditions, namely, high instantaneous conversion and relatively high levels of gel content.[41]

Surprisingly, Figure 5 shows that the use of a diacrylate monomer as cross-linker increased significantly the % Cq. It is possible that the increase of the % Cq was related to the autodeceleration effect that has been reported in the kinetics of cross-linking polymerization.[18,34,42,43] Such autodeceleration occurs when the propagation reactions also becomes diffusion limited because monomers and unreacted double bonds diffuse slowly through the growing polymer network. In the polymerization of BA, this decrease would enhance the backbiting rate and hence the increase of quaternary carbon formation.

Furthermore, an important increase of % Cq during the cooking period was observed in Figure 5. In approximately 3% monomer conversion, % Cq increased significantly for the shorter diacrylates, EGDA, BDA, and HDDA, and less for the longer, PEGDA. As in the case of the homopolymerization of BA,[39,40,45,46] backbiting is likely the predominant mechanism for Cq formation during the copolymerization with cross-linkers. However, the 1% increased observed in Cq level during the cooking period would have required the maximum achievable backbiting rate (one backbiting event every three propagation steps) to occur during this period, which does not seem likely. Therefore, other mechanisms should be responsible for this sudden increase during the cooking period.

Kloosterboer[34] studied the formation of tertiary radicals, especially in the photopolymerization of multifunctional monomers (1,6-hexanediol diacrylate) by means of ESR spectroscopy, reporting that although the radicals which are hooked up to the network can hardly diffuse, hydrogen transfer introduces some mobility of the radical sites in the polymer. Because of this mobility, the tertiary radicals may terminate by combination with another tertiary radical present in the network as illustrated in Figure 6, yielding two quaternary carbons. This mechanism may explain the increase of branching density (Cq) observed during the cooking period (Figure 5).

Figure 7 and Table 3 present the evolution of the swelling for the latexes obtained with 2.3 mol % of the diacrylates and the swelling values for all the final latexes, respectively. The swelling value of a polymer is inversely proportional to the cross-linking density,[49] namely, the more cross-linked the polymer, the less its swelling capability. Table 3 shows that the latexes prepared with the diacrylates were more cross-linked (lower swelling value) than the homopolymer of BA. In addition, latexes with EGDA and BDA had a similar cross-linking density evolution whereas the longer cross-linkers (HDDA and PEGDA) yielded a higher cross-linking density from the very beginning of the reaction.

This behavior can be explained by the different tendency that the pendant double bonds resulting from the cross-linkers show for intramolecular cyclization and cross-linking reactions. In this series of cross-linkers, the reactivity of the double bonds is the same in all the cases as they all are symmetric diacrylate monomers. However, the mobility and the accessibility to the pendant double bonds (once the first double bond in the molecule has reacted) are not the same as the separation of the pendant double bond from the main chain increases with the length. The swelling results of Figure 7 and the mechanical properties presented in Table 4 and Figure 9 suggest that the cross-linking reaction is favored over the cyclization for the longer diacrylates (lower swelling and higher the modulus in the rubbery region). Other authors[25,26] have shown, in similar cross-linking batch bulk copolymerizations, that gelation was delayed and that cross-linking density was higher for the longer diacrylates. Kannurpatti et al.[25] attributed the higher tendency toward cyclization of the shorter diacrylates to the higher probability for the radical center of the first double bond consumed to react with the close pendant double bond of the same diacrylate. (They pointed out that the pendant double bond is more diluted when the distance is longer.) The reaction between the radical center and the pendant double bond of the same cross-linker is one of the primary cyclization mechanisms. Primary cyclization may also occur when a growing radical reacts with a pendant double bond that does not belong to the repeating unit of the growing radical (Figure 8). Nevertheless, modeling of cross-

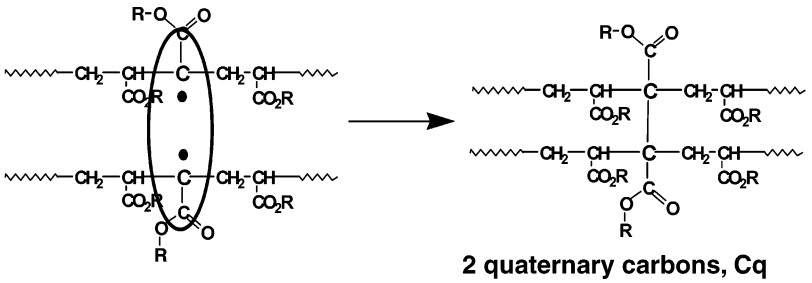

**Figure 6.** Structure resulting of the termination by combination of two-trapped acrylate radicals.

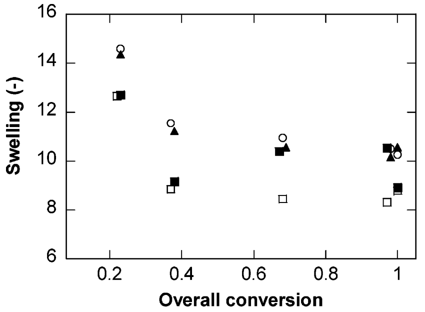

**Figure 7.** Evolution of the swelling for the seeded semicontinuous emulsion copolymerizations carried out with different diacrylates at 2.3 mol %. Legend: (○) BA/EGDA, (▲) BA/BDA, (■) BA/HDDA, and (□) BA/PEGDA.

**Table 4. Values of the $T_g$ (tan $\delta$), $G'$, and $M_e$ (Measured at the Minimum of tan $\delta$) for the Polymer Films from Latexes Produced with Diacrylates**

| run | $T_g$ (K) (tan $\delta$) | $G'$ (Pa) (min tan $\delta$) | $M_e$ (g/mol) (min tan $\delta$) |
|---|---|---|---|
| BA/BDA | 239 | $1.34 \times 10^5$ | 17 837 |
| BA/HDDA | 241 | $1.55 \times 10^5$ | 16 476 |
| BA/PEGDA | 242 | $2.50 \times 10^5$ | 10 000 |

linking polymerization that accounted for both possibilities[22,23,35,36,50] demonstrated that the reaction between the radical and the pendant double bond of the same cross-linker is the predominant primary cyclization mechanism. Therefore, the fraction of the pendant double bonds which is used for primary cyclizations and hence is not available for cross-linking decreases with the length of the cross-linker. This supports our observations that the longer the diacrylate, the more cross-linked (lower swelling values) the copolymer.

Figure 9 presents the sol $\overline{M_w}$ of samples taken during the seeded semicontinuous experiments carried out with 2.3 mol % of BDA and PEGDA, and Table 3 displays the final sol molecular weight for all the experiments carried out with the diacrylates. The sol polymer injected into the GPC was recovered from swelling experiments performed with these samples. It can be seen that in both cases the sol $M_w$ initially decreased to reach a plateau value and that the sol $M_w$ was the same for BDA and PEGDA. The sol $M_w$ of the polymerizations with cross-linker was significantly lower than that produced in the homopolymerization of BA due to the tighter network structure achieved with the cross-linkers that yield a more cross-linked polymer and hence larger amount of gel polymer. The sol MW decreases as gel increases because the longer chains are preferentially incorporated to the gel.

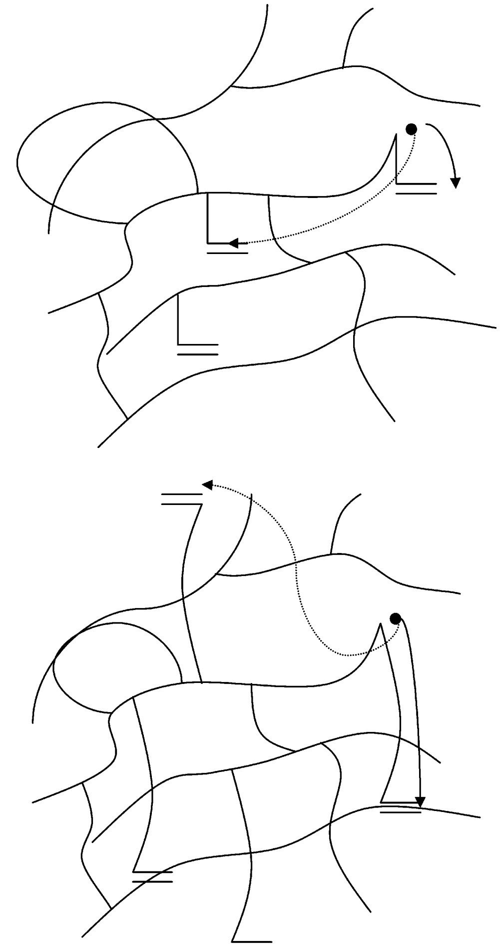

**Figure 8.** Primary cyclization reactions using diacrylates of different lengths. The solid arrows indicate the cyclopolymerization reaction and the dashed arrows the cyclization reaction with a pendant double bond not belonging to the growing radical monomer unit. The longer the diacrylate, the less probable are both cyclization reactions.

Dynamic mechanical analysis (DMA) was performed to measure the glass transition temperature, $T_g$, the storage modulus, $G_n°$, and molecular weight between cross-links, $M_e$, of the latexes prepared using the four cross-linkers. Kannurpatti et al.[25] and Elliot et al.[26] reported that enhanced primary cyclization caused a decrease of the $T_g$, a decrease of the storage modulus, $G_n°$, and thus an increase of the molecular weight between cross-linking points, $M_e$, of the copolymers. This effect was stronger as the concentration of cross-linker increased.

Table 4 shows the values of the $T_g$, the storage modulus, and the average molecular weight between cross-links, $M_e$, for the experiments carried out with the diacrylates. It can be seen that the values of the $T_g$ slightly increased as the length of the diacrylates increases that mean that the networks were more cross-linked, which is in agreement with swelling experiments.

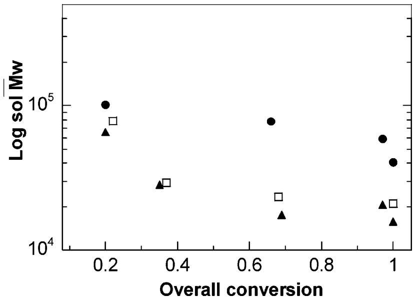

**Figure 9.** Evolution of the sol weight-average molecular weight for the seeded semicontinuous emulsion copolymerizations carried out with BDA and PEGDA at the concentration of 2.3 mol %. Legend: (●) BA, (▲) BA/BDA, and (□) BA/PEGDA.

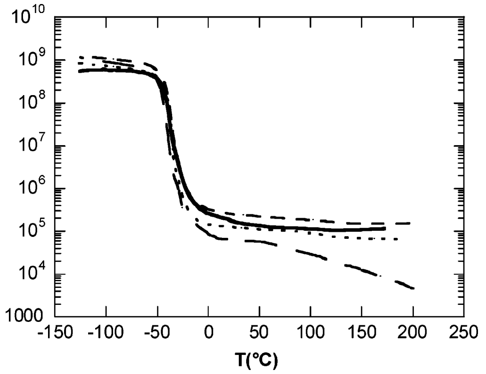

**Figure 10.** Isochronal temperature dependence of the storage modulus, $G'$, recorded for the polymer films of the seeded semicontinuous emulsion copolymerizations carried out with different diacrylates at 2.3 mol %. Legend: (— — —) BA, (• • •) BA/BDA, (—) BA/HDDA, and (- - -) BA/PEGDA.

Figure 10 shows the isochronal temperature dependence of the storage modulus ($G'$). The $G'$ value in the rubbery state and the value of $M_e$ calculated from eq 1 are given in Table 4. It can be seen that the shorter the cross-linker chain length, the lower the storage modulus and the higher the $M_e$, namely, the lower the cross-linking density.

## Conclusions

The effect of the ester size of diacrylates on the kinetics of the seeded semicontinuous polymerization of BA and on the microstructural and mechanical properties of the polymers was studied. The results showed that, contrary to what it was reported in batch bulk polymerizations, the length of the ester size did not have an effect on kinetics, probably because the polymerization proceeded under starved conditions and polymerization rate was controlled by the monomer feeding rate. In addition, the amount of gel polymer and the sol molecular weight were not significantly affected by the length of the ester size of the cross-linker. On the other hand, the number of quaternary carbons, the cross-linking density, and the mechanical properties of the films were strongly affected by the length of the ester chain. The shorter the diacrylate, the less cross-linked the polymer, the lower the $T_g$ and the storage modulus, and the higher the average molecular weight between entanglements.. The results were explained in terms of an enhanced primary cyclization over cross-linking reactions for the shorter diacrylate cross-linkers.

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## References and Notes

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