ELSEVIER

Chemical Engineering Journal 122 (2006) 117–126

Chemical Engineering Journal

www.elsevier.com/locate/cej

Continuous production of specialty waterborne adhesives: Tuning the adhesive performance

F. Alarcia, J.C. de la Cal, J.M. Asua*

Institute for Polymer Materials (POLYMAT) and Grupo de Ingeniería Química, Departamento de Química Aplicada, Facultad de Ciencias Químicas, The University of the Basque Country, Apdo. 1072, 20080 Donostia-San Sebastián, Spain

Received 16 January 2006; received in revised form 12 May 2006; accepted 22 May 2006

Abstract

The possibility of tuning the adhesive performance of all-acrylic waterborne adhesives produced in a continuous stirred tank reactor (CSTR) was investigated by manipulating the conditions in the holding tank.

The effect of the holding tank temperature, the addition of different types of chain transfer agents and the post-polymerization using different initiator systems was investigated. It was observed that the holding tank temperature had a significant effect on polymer architecture, which in turn led to different adhesion performance. The water-solubility of the chain transfer agents, as well as the production time at which the addition was performed were found to be crucial controlling the polymer structure. An early shot at 10% of the total production, combined with a water-soluble CTA led to important changes in polymer structure and therefore on its adhesion performance. Post-polymerization was found to be effective in monomer removal. The choice of the initiator system was another means to modify the polymer structure and hence a possible way to extend the range of properties achievable with the given base emulsion polymer produced in the CSTR.

Keywords: Continuous reactors; Waterborne adhesives; Emulsion polymerization; Adhesive performance

1. Introduction

Pressure sensitive adhesives (PSAs) are viscoelastic materials that can adhere strongly to a wide variety of substrates by application of slight pressure under short periods of time [1–3]. These kind of materials are commonly produced in semi-continuous emulsion polymerization. The high flexibility of these reactors allows the production of adhesives with fine-tuned adhesive performance [4,5]. However, the increasingly demand of these products and the strong competitions among producers is leading to increase the productivity of the plants. This goal might be achieved by replacing the semi-continuous reactors by continuous systems, which besides increasing significantly the production per unit volume of reactor may improve reproducibility, a commonly encountered problem in the semi-continuous reactors. Despite the many potential advantages related to continuous systems, their flexibility is a major concern. The flexibility of a system is the possibility of quickly adapt to changes in production to meet the requirements and expectations of customers. For specialty products as PSAs, this means the ability of producing different products in the same reactor. The straightforward way of producing different products in a CSTR is to vary the composition of the feed. Because of the characteristic residence time distribution of the CSTRs, off-spec products are always produced during grade transitions. Nevertheless, it has been reported [6,7] that a 300 L CSTR was able to produce seven different grades per week with an overall production of 280 t/week (i.e., including a grade transition per day) under safe conditions with a limited amount of transition product. Following the adequate strategy the transition product may be blended with the main products without a delirious effect on quality. The experimental unit consisted in a CSTR and a holding tank, where the product leaving the CSTR was stored. The holding tank allowed to reach complete conversion, which cannot be achieved in the CSTR.

The performance of waterborne adhesives strongly depends on the polymer architecture (gel fraction and molecular weight) [8], which in all-acrylic emulsion polymerization is largely determined in the final stages of the polymerization [9], namely those carried out in the holding tank. This opens the possibil-

---

* Corresponding author. Tel.: +34 943018181; fax: +34 943015270.
E-mail address: jm.asua@ehu.es (J.M. Asua).

1385-8947/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2006.05.015

ity of tuning the adhesive performance (i.e., producing different adhesive grades) of all-acrylic waterborne adhesives by manipulating only the conditions in the holding tank. This process would lead to virtually no grade transition products.

2. Experimental

2.1. Materials

Monomers 2-ethyl hexyl acrylate (2EHA), methyl methacrylate (MMA) and acrylic acid (AA) were used as received without further purification. The surfactant used was Dowfax 2A1 (45 wt.% active) from Dow Chemical. Sodium hydrogen carbonate (Panreac) was used as buffer and ammonium persulfate (Merck)/sodium bisulphite (Merck) and *tert*-butyl hydro peroxide (Merck)/ascorbic acid (Aldrich) as redox initiator systems. The chain transfer agents used were *n*-dodecyl mercaptan and *tert*-dodecyl mercaptan (Fluka). Deionized water was used in all the reactions. Hydroquinone (Merck) was used for stopping the reaction in the samples withdrawn from the reactor and from the holding tank, and tetrahydrofurane (THF, analytical grade from Panreac) was used to extract the soluble part of the polymer samples.

2.2. Continuous emulsion polymerizations

Continuous emulsion polymerizations were carried out in a 0.3 L CSTR equipped with a combination of a Rushton six-blade turbine impeller in the lower part of the reactor and a two-blade (45° inclined) stirrer in the upper part. The polymerizations were carried out using the formulation presented in Table 1, a reactor temperature of 80 °C; a stirring rate of 260 rpm and a residence time of 10 min. The pre-emulsion feed consisting of the monomers, the emulsifier and 70% of total amount of water was continuously stirred and purged with nitrogen. The purge started 1 h before the beginning of the process. No nitrogen was used in the reactor. The process was started-up with the reactor completely filled with a latex synthesized in a previous polymerization and was run with the reactor completely filled, i.e., without headspace. The resulting latex was collected in a stirred holding tank kept under nitrogen atmosphere. The temperature in the holding tank was controlled by means of a thermostatic bath.

Table 1
Formulation used for in the continuous reactions ($T_{\mathrm{CSTR}} = 80\,^{\circ}\mathrm{C}$; $\tau = 10$ min)

	Parts per 100 parts of monomer
Solids content (wt.%)	50
Monomers	
2EHA	80
MMA	19
AA	1
Emulsifier	
Dowfax 2A1	3.33 (1.5 active)
Initiator	
$(NH_4)_2S_2O_8/Na_2S_2O_5$	2 (55/45)
Buffer	
$NaHCO_3$	0.5

2.3. Latex characterization

Samples withdrawn from the reactor and from the holding tank were short-stopped with a hydroquinone solution (1 wt.%), and the conversion was determined gravimetrically.

The gel content was defined as the fraction of polymer that was not soluble in THF at 70 °C. It was measured by soxhlet extraction and the results obtained were double checked by means of a Cohen-Addad's [10] modified method in which the extraction of the soluble part of the polymer was carried out in a glass reactor using THF under reflux during 8 h. The gel content, which corresponds to the non-soluble part, was calculated as follows:

$$\text{Gel content} = \frac{W_3 - W_1}{W_2 - W_1} \tag{1}$$

where W_1 stands for the initial weight of the filter, W_2 for the weight of the filter including the dried amount of polymer and W_3 for the weight of the final filter after extraction.

The molecular weight of the sol was determined by size exclusion chromatography (SEC). The samples were filtered (polyamide, $\Phi = 0.45\ \mu$m) before injection into the SEC instrument, which consisted of a pump (Waters Model 510), three columns (Styragel of porosity 102, 104 and 106 Å) and a dual detector system formed by a differential refractometer and a viscometer (Viscotek Model 250). The sol MWDs were obtained at 35 °C using a THF flow rate of 1 mL/min.

2.4. Adhesive properties

The quality of the latex produced was assessed by checking the adhesive performance of the PSAs produced. Tack, resistance to peel and resistance to shear were evaluated. Tack was assessed by using the rolling ball tack test [11]. This test consists of releasing a stainless-steel ball at the top of an inclined track, to come in contact at the bottom of the track with a horizontal upward-facing adhesive. The ball roll-out distance gives an inverse scale of tack, i.e., the longer the distance the ball travels across the adhesive before stopping the lower the tack.

Peel resistance was assessed by means of the 180° peel test [12]. In this test, a tape is applied to a standard metallic panel and the free end is clamped to the upper jaw of an Instron Tensile Tester, which pulls the tape at a constant speed of 300 mm/min. In this test, the average force required to peel away the tape is recorded.

Shear resistance was assessed by the holding power shear test [13]. This test consists in applying a standard area of tape on a panel holding 1 kg until failure. Initial tests were performed at room temperature but it was found that very long times were required for the adhesive to fail. Therefore, the failure was accelerated by performing the tests in an oven at 90 °C [14].

The adhesive films used in the tests were obtained by spreading the latex over a flame treated polypropylene 29 μm thick using a wire rod no. 5. The films were dried in an oven at 50 °C during 20 min, and were then allowed to cool down at room temperature for 20 min before being cut into the desired dimensions for each standard test.

3. Results and discussion

3.1. Effect of the holding tank temperature

The effect of the holding tank temperature was studied by keeping the conditions in the CSTR constant and varying the holding tank temperature. Reactions were carried out in a single CSTR at 80 °C, using a residence time of 10 min. The recipe used in these reactions is given in Table 1. Fig. 1 shows the evolution of conversion both in the CSTR (solid symbols) and in the holding tank (empty symbols) for four different runs in which the holding tank temperature was varied from 40 to 75 °C. The CSTR was operated for about 150 min and the conversion in the holding tank was monitored for a longer period. It can be seen that the conversion in the CSTR was about 80%, whereas almost complete conversion was achieved in the holding tank. The oscillations in conversion in the CSTR are typical of emulsion polymerization in a CSTR [15] and are due to intermittent particle nucleation [16,17].

Fig. 2 presents the evolution of gel fraction in samples taken from the holding tank during the batch period. In this plot, $t = 0$ represents the moment in which the CSTR operation ceased. As a reference, Fig. 2 also includes the gel fraction measured at the exit of the CSTR (solid symbols). It can be seen that the amount of gel substantially increased in the holding tank and that the higher the holding tank temperature the higher the amount of gel. The reason for this increase is that the activation energy for propagation is lower than those for chain transfer reactions to polymer, and therefore the transfer reactions are favoured at higher temperatures, leading to the formation of a higher amount of gel [18]. Fig. 2 also shows that the gel fraction did not significantly vary after the cease of the operation of the CSTR. This was due to the combination of two reasons. First, no additional monomer arrived to the holding tank and hence monomer concentration quickly approached zero. This drastically reduced the formation of new links between macromolecules by propagation and subsequent termination. In addition, the lack of monomer severely reduced radical entry [19]. The redox system used in this work produces negatively charged radicals in the aqueous phase that are very hydrophilic. Therefore, in order enter into the polymer particles, they should be rendered hydrophobic by polymerization with monomer in the aqueous phase. The absence of monomer made that most of the radicals produced terminated in the aqueous phase. The second reason was that a redox system was used. These systems yield a high radical generation rate, but they have a very short live time. Therefore, shortly after the cease of the CSTR operation the initiator concentration in the holding tank approached to zero.

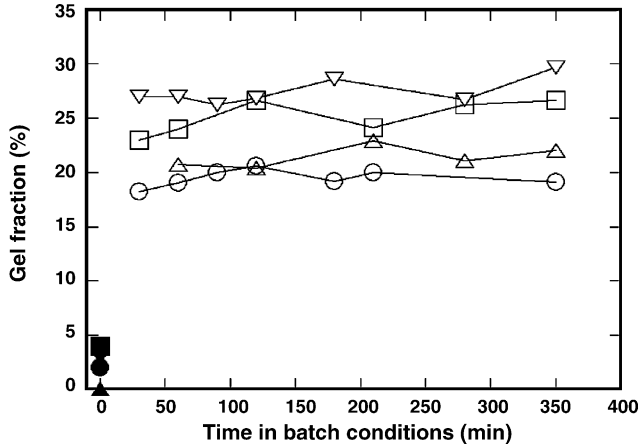

Fig. 2. Evolution of gel content of the polymer in the holding tank for different temperatures (the solid dots indicate the gel fraction in the CSTR just before interrupting the continuous process—about 150 min in Fig. 1): (● and ○) −40 °C; (▲ and △) −50 °C; (■ and □) −65 °C; (▼ and ▽) −75 °C.

The sol molecular weight distribution of the polymers produced using different holding tank temperatures are presented in Fig. 3. It can be seen that the polymer produced at the lowest temperature presented the highest sol molecular weight, but no apparent effect was observed for temperatures higher than 50 °C. Based on the results reported for the conventional semi-continuous system, the latter result is surprising. In a semi-continuous reactor, high temperatures result in high instanta-

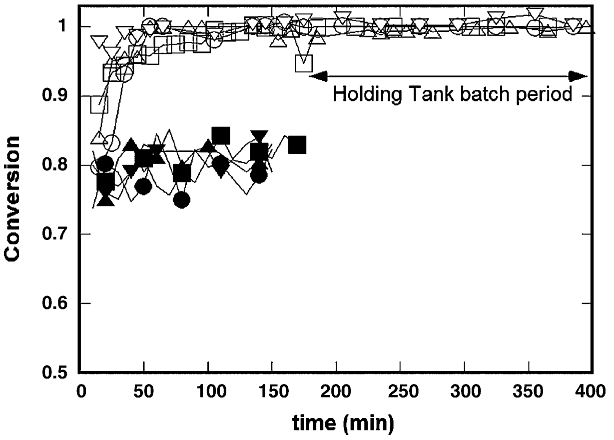

Fig. 1. Evolution of conversion both in the CSTR (solid dots) and in the holding tank (empty symbols) as a function of holding tank temperature: (● and ○) −40 °C; (▲ and △) −50 °C; (■ and □) −65 °C; (▼ and ▽) −75 °C.

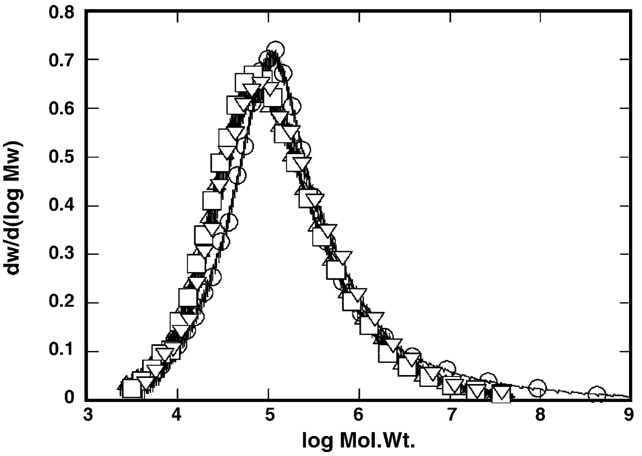

Fig. 3. Sol molecular weight distribution of the polymers produced at different holding tank temperatures: (○) −40 °C; (▽) −50 °C; (□) −65 °C; (▽) −75 °C.

neous conversions, i.e., low monomer concentrations, which in turn enhance chain transfer to polymer that when followed by termination by combination leads to gel formation [20,21]. This effect is enhanced by the higher activation energy of chain transfer to polymer as compared to that of the propagation. Because the likelihood of suffering intermolecular chain transfer is proportional to the chain length, long macromolecules are preferentially incorporated into the gel [18]. Therefore, one would expect that the higher the gel content the lower the sol molecular weight. In addition, in a semi-continuous process high temperatures resulted in shorter kinetic lengths. As a consequence of the two effects, when temperature increases a decrease in sol molecular weight is expected in those reactors [21]. However, the current process is completely different from the conventional semi-continuous operation. First, most of the polymer (about 80%) was formed under the same conditions in the CSTR. This base polymer was then partially modified in the holding tank. The modification was apparently in the terms of gel fraction but not so in terms of the sol molecular weight distribution. One reason for the different sensitivities of these measurements may be that whereas the gel fraction increased by a 30% (relative values) from 50 to 75 °C the amount of sol polymer was only reduced by 10%. Therefore, the sol polymer only differed in a relatively small fraction of the high molecular weight chains. In addition, the effect of temperature on the kinetic length in the holding tank was modest. In a conventional free radical polymerization, the kinetic length decreases with temperature mostly because the rate of radical formation increases faster than the propagation rate. As termination is proportional to the second power of the radical concentration, the increase in radical concentration yields to a higher termination probability, namely to shorter chains. However, the situation in the holding tank was different. The initiator that arrived to the holding tank was the fraction of the redox system that survived the CSTR. Considering the short live time of the redox initiators, this fraction was likely small and it readily reacted in the holding tank. Therefore, the increase of temperature in the holding tank had only a moderate effect on the kinetic length of the polymer formed in the holding tank (about 20% of the whole polymer).

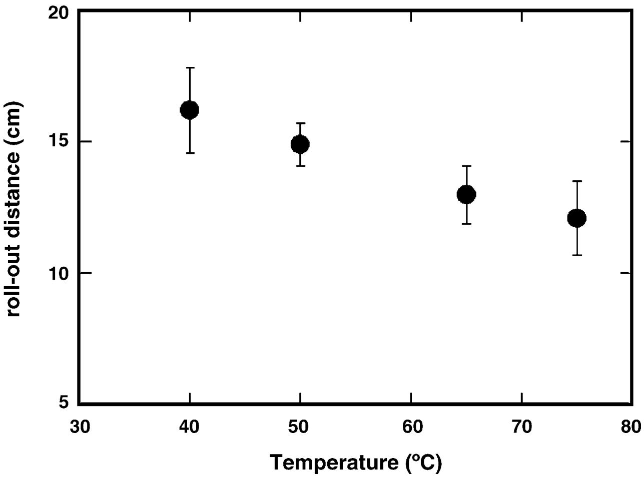

Fig. 4. Influence of the holding tank temperature on tack.

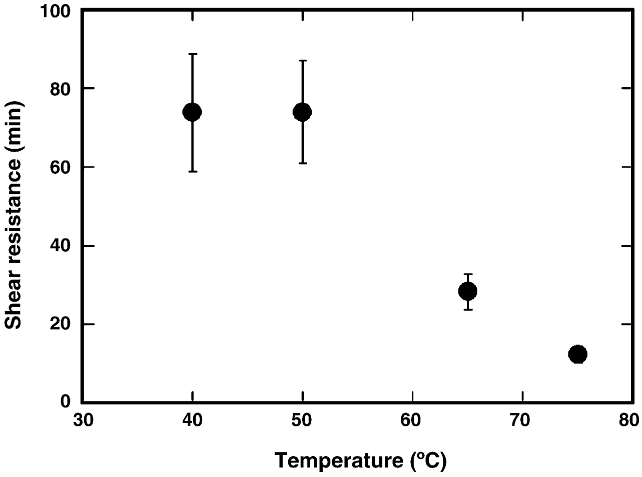

Fig. 5. Influence of the holding tank temperature on shear resistance.

Fig. 4 shows the influence of the holding tank temperature on tack. It can be seen that tack slightly increased with temperature. This suggests that the tack test was more sensitive to the moderate effect of the temperature on the kinetic length than the sol MWD measurements. Fig. 5 shows that shear resistance sharply reduced with temperature. Likely, the reason was that high gel fractions may hinder particle–particle interpenetration during film formation [22], leading to the formation of films with lower cohesive strength. Fig. 6 shows that the holding tank temperature had almost no effect on peel resistance. Peel resistance is known to be influenced by the middle range molecular weights of the polymers [23], which in the present case were produced in the CSTR, and hence they were present in all samples.

3.2. Effect of the addition of chain transfer agents in the holding tank

The presence of chain transfer agent (CTA) strongly affects the architecture of the acrylic polymers [24–26]. Therefore, the effect of adding CTAs to the holding tank was investigated. Two experiments were carried out adding a shot of *n*-dodecyl mercaptan to the holding tank. In the first one, the shot was injected

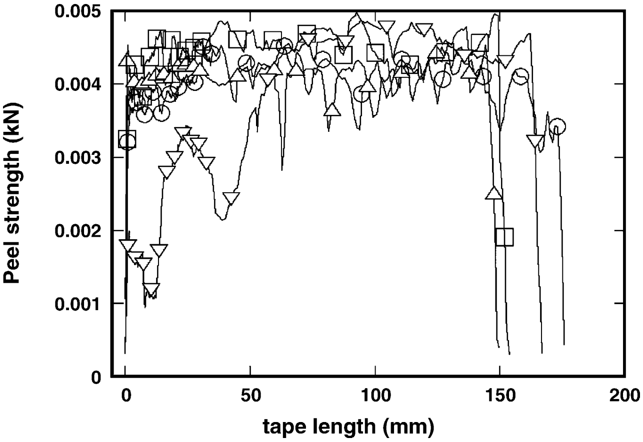

Fig. 6. Influence of the holding tank temperature on peel resistance: (○) −40 °C; (△) −50 °C; (□) −65 °C; (▽) −75 °C.

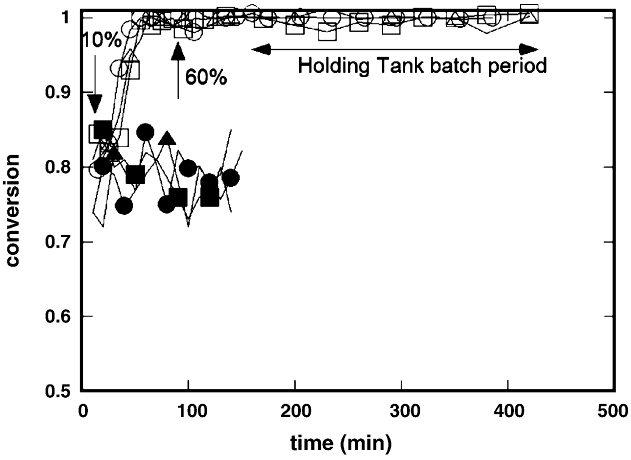

Fig. 7. Evolution of conversion as a function of time in the CSTR (solid dots) and in the holding tank (empty dots) for the runs with no CTA and with 0.06 wt.% of *n*-dodecyl mercaptan added at 10 and 60% of total production (holding tank temperature: 40 °C): (● and ○) no CTA; (■ and □) CTA added at 10% of total production; (▲ and △) CTA added at 60% of total production.

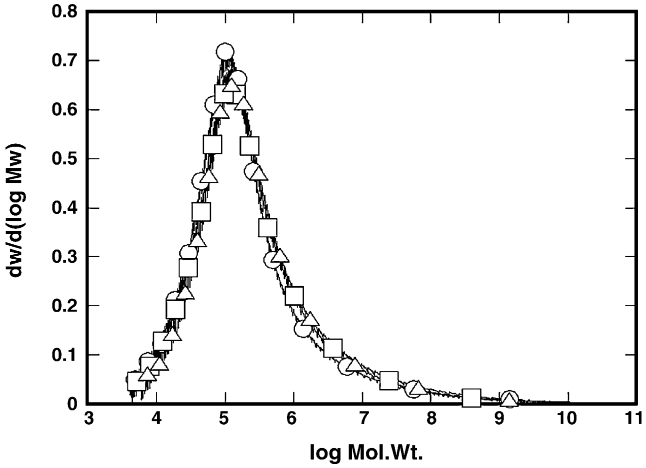

Fig. 9. Effect of *n*-dodecyl mercaptan addition on the sol molecular weight distribution: (○) no CTA; (□) CTA added at 10% of total production; (△) CTA added at 60% of total production.

when the amount of polymer in the holding tank was 10% of the total production ($t = 14$ min). In the second, the CTA was added at 60% of the total production ($t = 84$ min). The temperature in the holding tank was 40 °C.

Fig. 7 shows the evolution of conversion as a function of time both in the CSTR and in the holding tank for these reactions, as well as for a reaction in which no CTA was used. It is worthwhile pointing out that the operation in the CSTR was not affected in those experiments. It can be seen that the addition of CTA to the holding tank had no effect on monomer conversion.

Fig. 8 shows the final gel content obtained in these three reactions. It can be seen that the usage of CTA reduced drastically the fraction of gel. In addition, Fig. 8 suggests that the addition procedure may be a good way to fine-tune the fraction of gel.

Fig. 9 shows the sol molecular weight distribution of these polymers. Despite the differences obtained in the gel fraction, the molecular weight distribution was not affected by the presence of the chain transfer agent. The relative insensitivity of the sol molecular weight distribution to the presence of CTA has been reported in the semi-continuous emulsion polymerization of *n*-butyl acrylate [27]. The reason given was that the presence of CTA severely reduced gel, and hence the long polymer chains remained in the sol, compensating the reduction in the kinetic chain length. The same mechanism may be operative in the present case, although the lack of sensitivity is more acute than for the semi-continuous process. The fact that only a small fraction of the polymerization (about 18% when *n*-dodecyl mercaptan was fed at $t = 14$ min; and about 8% when it was fed at $t = 84$ min) was carried out in the presence of CTA might help to disguise the effect of *n*-dodecyl mercaptan on the sol MWD. However, there might be another reason for the lack of effect of *n*-dodecyl mercaptan on sol MWD. This CTA is rather water-insoluble and its transport to polymer particles is diffusionally limited [28,29]. Therefore, it was decided to check the effect of a more water-soluble chain transfer agent: *tert*-dodecyl mercaptan. This CTA was added at 10% of the production ($t = 14$ min) and pre-emulsified to accelerate the mass transfer. Fig. 10 shows the evolution of conversion in the CSTR and in the holding tank in this reaction. For the sake of comparison Fig. 10 also includes the monomer conversion evolution in similar polymerizations carried out without CTA and with *n*-dodecyl mercaptan.

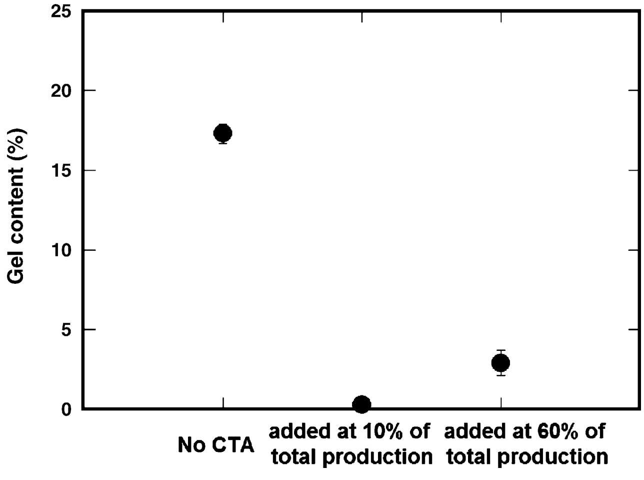

Fig. 8. Influence of *n*-dodecyl mercaptan addition on gel fraction.

Fig. 10 shows that the polymerization rate in the holding tank was lower when *tert*-dodecyl mercaptan was used. This decrease was attributed to the enhanced radical exit rate provoked by the formation of relatively water-soluble *tert*-dodecyl mercaptan radicals. This might reduce the number of radicals per particle and therefore the polymerization rate.

Fig. 11 shows that both chain transfer agents reduced the gel content to nil.

Fig. 12 presents the sol molecular weight distributions. It can be seen that *tert*-dodecyl mercaptan substantially reduced the sol molecular weight, probably due to lower diffusional limitations resulting from its higher water-solubility and the use of pre-emulsification. The adhesive properties of the latex produced using the CTAs are presented in Figs. 13 and 14. It can be seen that shear resistance sharply decreased when the gel content decreased. Combination of these results with those in

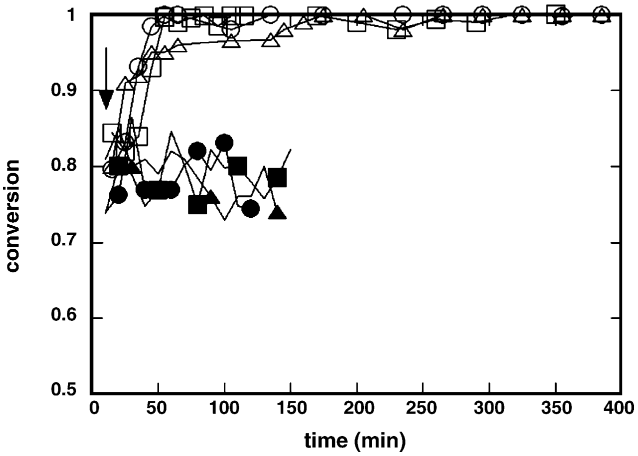

Fig. 10. Evolution of conversion in the CSTR (solid dots) and in the holding tank (empty dots) for the runs with no CTA and with 0.06 wt.% of *n*-dodecyl mercaptan and *tert*-dodecyl mercaptan added at 10% of the total production (holding tank temperature: 40 °C): (● and ○) no CTA; (■ and □) *n*-dodecyl mercaptan added at 10% of total production; (▲ and △) *tert*-dodecyl mercaptan added at 10% of total production.

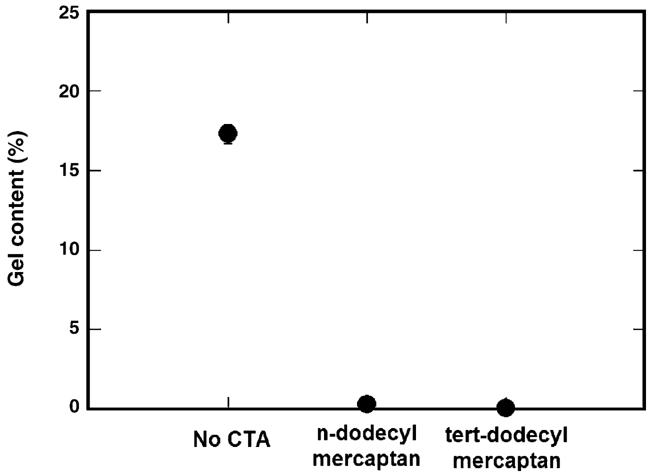

Fig. 11. Effect of the type of chain transfer agent on the gel fraction.

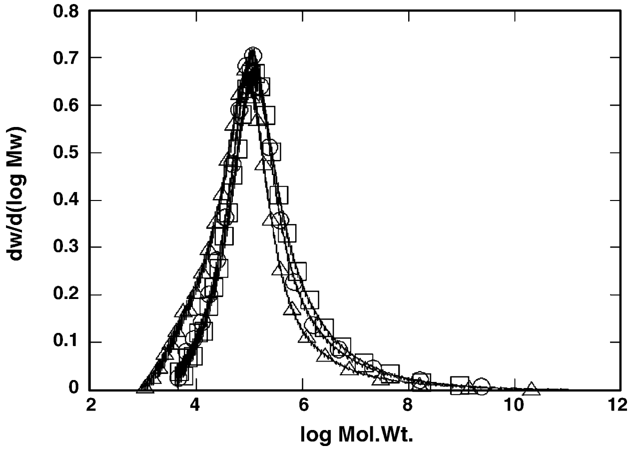

Fig. 12. Effect of the type of chain transfer agent on the sol molecular weight distributions: (○) No CTA; (□) *n*-dodecyl mercaptan added at 10% of total production; (△) *tert*-dodecyl mercaptan added at 10% of total production.

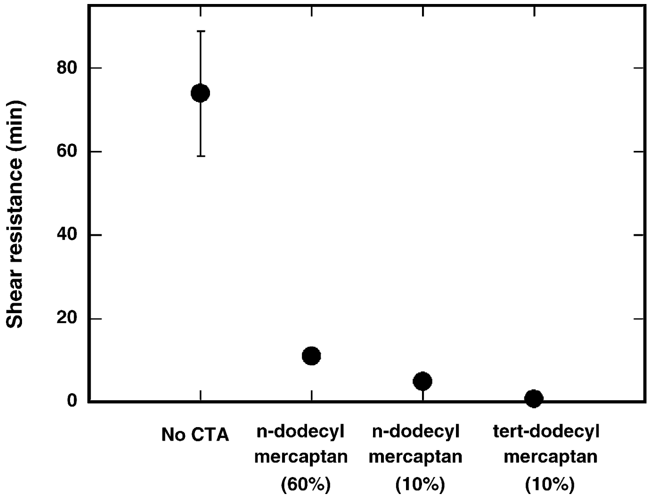

Fig. 13. Effect of the type of chain transfer agent on shear resistance.

Figs. 2 and 5 showed that a certain fraction of gel is necessary to built enough mechanical strength in the adhesive film [30], but when the gel fraction exceeded some threshold the gel hindered the polymer particles interdiffusion during film formation leading to a mechanically weak film. The results reported in this work showed that the shear resistance can be fine-tuned by controlling the conditions in the holding tank. Fig. 14 shows that the low molecular weights produced with *tert*-dodecyl mercaptan led to a more tacky film. Fig. 15 shows that peel strength significantly decreased with the reduction of both sol molecular weight and gel content.

3.3. Effect of adding initiators to the holding tank

Figs. 1, 7 and 10 show that almost complete conversion was achieved in the holding tank. However, analysis of these latexes by gas chromatography showed that the amount of residual monomer (2EHA, as no traces of the more reactive MMA were detected) was in the range of 1500–2200 ppm. This amount

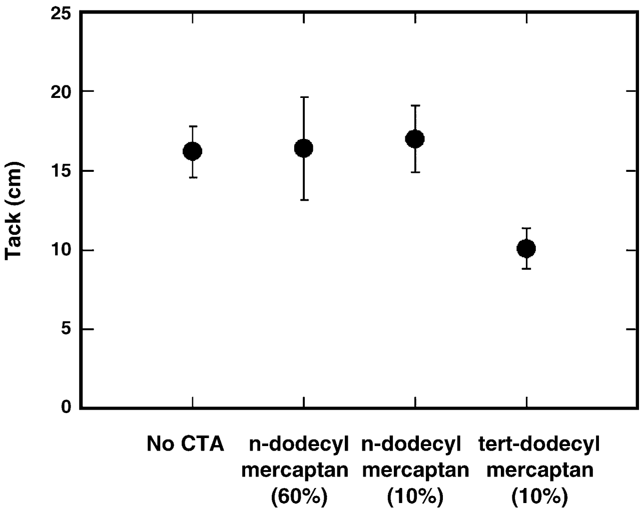

Fig. 14. Effect of the type of chain transfer agent on tack.

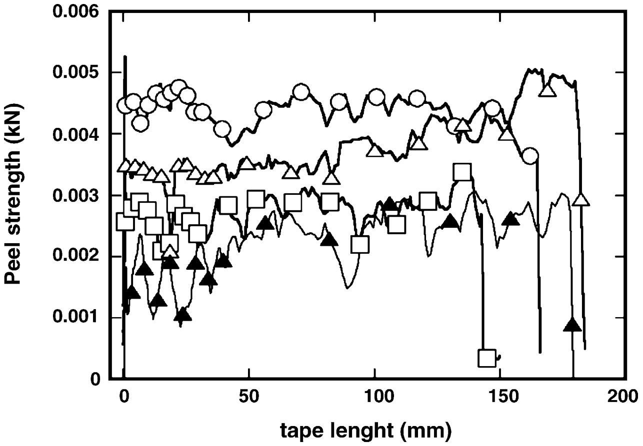

Fig. 15. Effect of CTA type and addition procedure on peel resistance: (○) No CTA; (△) *n*-dodecyl mercaptan added at 60% of total production; (□) *n*-dodecyl mercaptan added at 10% of total production; (▲) *tert*-dodecyl mercaptan added at 10% of total production.

of residual monomer would be unacceptable for a commercial product. In order to reduce the amount of residual monomer to acceptable levels the latexes were post-polymerized. On the other hand, it is known that the type of initiator affects both the post-polymerization efficiency [19] and the polymer architecture [31]. Two initiator systems were used: ammonium persulfate (APS)/sodium bisulfite (SBS) and *tert*-butyl peroxide (TBPH)/ascorbic acid (Asc. Ac.). The polymers used in this study were obtained using holding tank temperatures of 40 and 75 °C. The post-polymerizations were carried out at 80 °C. The initiator system was fed during 30 min, and then the latexes were maintained at 80 °C for 60 min. Table 2 summarizes the results obtained in these post-polymerizations. It can be seen that both APS/SBS and TBPH/Asc. Ac. were very efficient for monomer removal reducing the monomer concentration to less than 100 ppm. The redox system producing hydrophobic radicals (TBHP/Asc. Ac.) seemed to be more efficient for both latexes presumably because of the higher efficiency of entry of those radicals [19,31]. The stability of the latexes was not affected by post-polymerization (same particle size before and after post-polymerization). Fig. 16 shows the gel content for both latexes before and after post-polymerization. It can be seen that by using APS/SBS the amount of gel remained constant whereas it increased when TBPH/Asc. Ac. was used. This was due to the different type of radicals entering the polymer particles. *tert*-Butoxyl radicals are hydrophobic, and hence they readily enter into polymer particles. They are oxygen-centered which are very efficient abstracting labile hydrogens from the tertiary carbons of the polymer chains producing quaternary radicals. Bimolecular termination of these radicals leads to gel formation [31]. Sulfate radicals are also oxygen-centered but are too hydrophilic and must react with monomer to be able to enter into polymer particles. However, carbon-centered oligoradicals are less efficient for hydrogen abstraction.

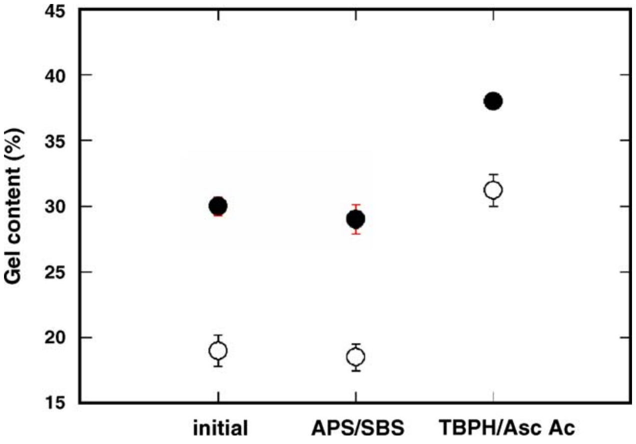

Fig. 16. Effect of post-polymerization with APS/SBS and TBPH/Asc. Ac. on gel fraction: (●) latex produced with a HT temperature of 75 °C; (○) latex produced with a HT temperature of 40 °C.

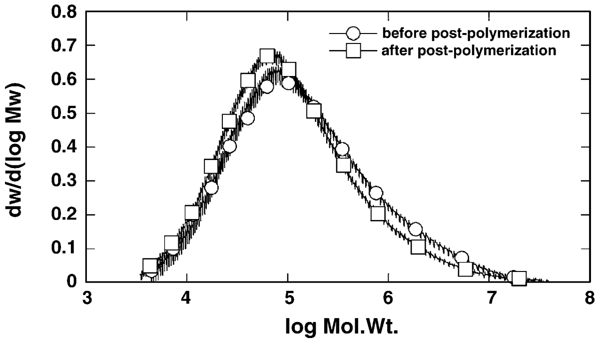

Fig. 17. Effect of post-polymerization with APS/SBS on the sol molecular weight distribution of the latex produced with a holding tank temperature of 40 °C: (○) before post-polymerization; (□) after post-polymerization.

Figs. 17 and 18 show the sol molecular weight distributions of the latex produced using a holding tank temperature of 40 °C before and after post-polymerization with APS/SBS and TBPH/Asc. Ac., respectively. It can be seen that when APS/SBS was used no significant changes in the sol molecular weight distribution was observed. On the other hand, when TBHP/Asc. Ac. was used, after post-polymerization, some high-molecular weight chains were incorporated to the gel,

Table 2
Results obtained in the post-polymerization of the latexes

Holding tank temperature	Initiator system	Amount (g)	Residual monomer 2EHA (ppm)		d_p (nm)	
			Initial	Final	Initial	Final
75 °C	APS/SBS	1.992/1.612	1770	64	279	277
	TBPH/Asc. Ac.	0.756/0.741	1638	32	278	280
40 °C	APS/SBS	1.992/1.612	2020	83	286	278
	TBPH/Asc. Ac.	0.756/0.741	2130	72	281	281

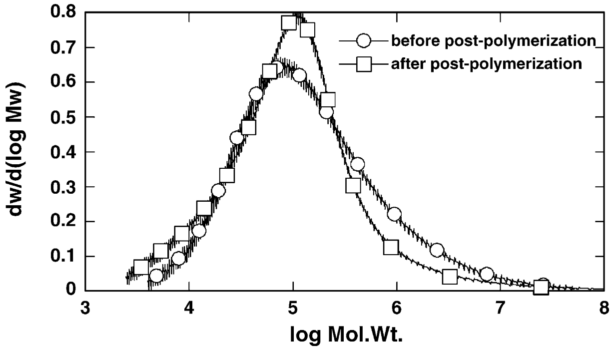

Fig. 18. Effect of post-polymerization with TBHP/Asc. Ac. on the sol molecular weight distribution of the latex produced with a holding tank temperature of 40 °C: (○) before post-polymerization; (□) after post-polymerization.

and therefore narrower molecular weight distributions were obtained.

Fig. 19 presents the effect of post-polymerization on tack. As gel is mainly formed from high molecular weight chains, the low molecular weight chains were not significantly affected by post-polymerization, and therefore tack was not influenced by this process.

Fig. 20 shows that whereas the post-polymerization with APS/SBS did not affected the shear resistance, the use of TBHP/Asc. Ac. severely decreased the shear resistance of the latex produced with a holding tank temperature of 40 °C. The reason was the increase in gel caused by TBHP/Asc. Ac. (Fig. 16). The effect of this initiator system on the shear resistance of the latex produced with a holding tank temperature of 75 °C was small because before post-polymerization, this latex already contained a gel fraction higher than the critical value. Fig. 21 shows that post-polymerization did not change significantly the peel resistance of the polymer produced with a holding tank temperature of 75 °C. On the other hand, Fig. 22 shows a slight increase of peel resistance after post-polymerization when the holding tank was maintained at 40 °C. The reason may be the low initial amount of gel (before post-polymerization) of the polymer produced using a holding tank temperature of 40 °C.

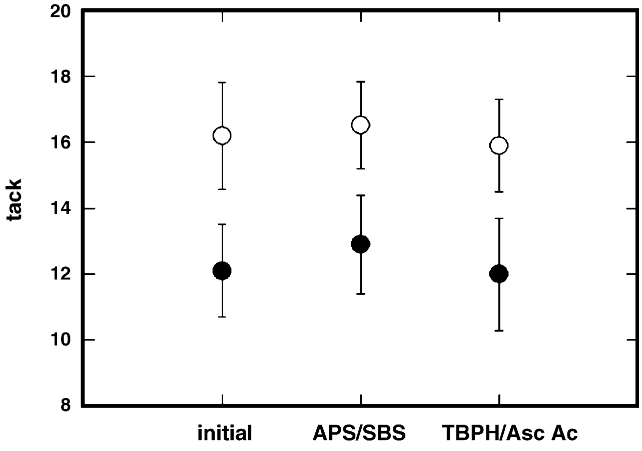

Fig. 19. Effect of post-polymerization with TBPH/Asc. Ac. on tack: (●) latex produced with a HT temperature of 75 °C; (○) latex produced with a HT temperature of 40 °C.

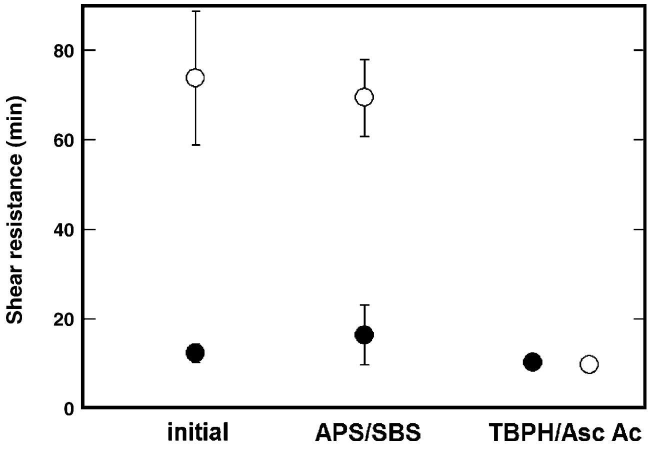

Fig. 20. Effect of post-polymerization with TBPH/Asc. Ac. on shear resistance: (●) latex produced with a HT temperature of 75 °C; (○) latex produced with a HT temperature of 40 °C.

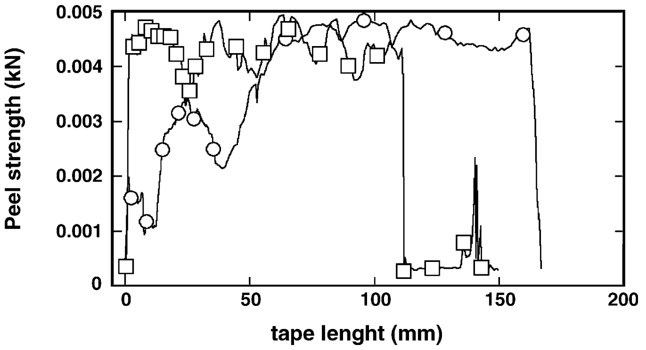

Fig. 21. Effect of post-polymerization with TBPH/Asc. Ac. on peel resistance of the latex produced using a holding tank temperature of 75 °C: (○) before post-polymerization; (□) after post-polymerization.

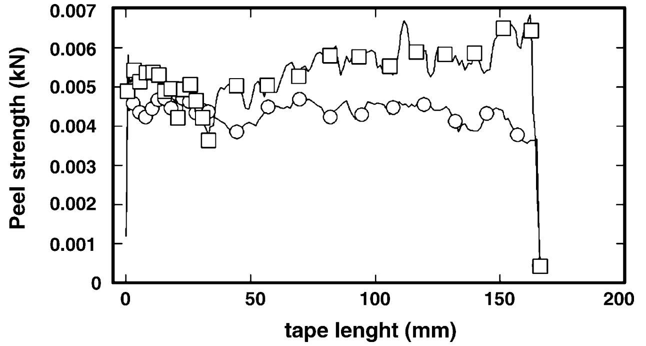

Fig. 22. Effect of post-polymerization with TBPH/Asc. Ac. on peel resistance of the latex produced using a holding tank temperature of 40 °C: (○) before post-polymerization; (□) after post-polymerization).

4. Conclusions

The feasibility of fine-tuning the performance of all-acrylic waterborne adhesives produced in a continuous process, by manipulating the conditions in the holding tank was investigated. The effects of the holding tank temperature, the addition of chain transfer agents to the holding tank and the post-polymerization process on the adhesion performance was studied. It was found that although nearly 80% of the total polymer was produced in the CSTR, the reaction conditions in the holding tank played a key role in the architecture of the final polymer, leading to substantial changes on the adhesive performance. It was found that higher temperatures in the holding tank resulted in an increase in the gel fraction, while the sol molecular weight was less sensitive. This changes in polymer structure affected the adhesive performance: while peel resistance remained nearly constant, tack increased and shear resistance decreased.

On the other hand, the effect of adding chain transfer agents was found to be dependent on their water solubility. *n*-Dodecyl mercaptan avoided the formation of gel, but almost no effect on the sol molecular weight was observed. Under these circumstances, shear resistance decreased but tack was not affected. It was found that the usage of a more water-soluble CTA, *tert*-dodecyl mercaptan, led to the formation of a polymer with no gel and lower molecular weight. As a consequence, besides decreasing the shear resistance, tack was improved. Moreover, it was found that shear resistance initially increased with gel fraction, but above a certain value of gel, the shear resistance decreased sharply, probably due to a poor interdiffusion among polymer particles during film formation, which led to mechanically weaker films.

Concerning post-polymerization, both APS/SBS and TBHP/Asc. Ac. were efficient for monomer removal, reducing the monomer concentration to less than 100 ppm. It was found that the hydrophobic radicals produced by TBHP/Asc. Ac. were more efficient for monomer removal. Both shear and peel resistances were changed by using TBHP/Asc. Ac. In addition, the adhesive properties were not significantly changed after post-polymerization using APS/SBS, due to its low effect on polymer structure. This study shows that a base polymer produced in a CSTR can be further manipulated in the holding tank in order to obtain final polymers with different adhesive performance opening the possibility to extend the range of properties achievable in the CSTR.

Acknowledgments

The authors acknowledge the financial support of the Industrial Liaison Program of Polymerization in Dispersed Media of Polymat (Arkema, Cytec—Surface Specialties, Euroresin—Química Europea de Resinas S.A., Nuplex Resins, Rohm and Haas, Wacker Polymer Systems).

References

[1] D. Tobing, A. Klein, Mechanistic studies in tackified acrylic emulsion pressure-sensitive adhesives, J. Appl. Polym. Sci. 76 (2000) 1965–1976.

[2] D. Tobing, A. Klein, Molecular parameters and their relation to the adhesive performance of acrylic pressure-sensitive adhesives, J. Appl. Polym. Sci. 79 (2001) 2230–2244.

[3] C. Creton, Pressure-sensitive adhesives: an introductory course, MRS Bull. 28 (2003) 434–439.

[4] J. Kanetakis, F.Y.C. Wong, A.E. Hamielec, J.F. MacGregor, Steady-state modelling of a latex reactor train for the production of styrene – butadiene rubber, Chem. Eng. Commun. 35 (1985) 123–140.

[5] O. Elizalde, M. Vicente, J.R. Leiza, J.M. Asua, Control of the adhesive properties of *n*-butyl acrylate/styrene latexes, Polym. React. Eng. 10 (2002) 265–283.

[6] F. Alarcia, J.C. de la Cal, J.M. Asua, Process intensification in the production of specialty waterborne polymers, Macromol. Mater. Eng. 291 (2006) 428–437.

[7] F. Alarcia, J.C. de la Cal, J.M. Asua, Scheduling the production of a portfolio of emulsion polymers in a single CSTR, Ind. Eng. Chem. Res. 45 (2006) 3711–3717.

[8] C. Plessis, G. Arzamendi, J.R. Leiza, H. Schoonbrood, D. Charmot, J.M. Asua, Kinetics and polymer microstructure of the seeded semibatch emulsion copolymerization of *n*-butyl acrylate and styrene, Macromolecules 34 (2001) 5147–5157.

[9] G. Arzamendi, J.M. Asua, Modeling gelation and sol molecular weight distribution in emulsion polymerization, Macromolecules 28 (1995) 7479–7490.

[10] J.P. Cohen-Addad, C. Bojonuk, V. Granier, Gel-like behavior of pH dependent latex films, Macromolecules 27 (1994) 5032–5036.

[11] American Pressure Sensitive Tape Council, Norm PSTC-6M, Tack Rolling Ball, 1986.

[12] American Pressure Sensitive Tape Council, Norm PSTC-1M, Resistance to peel for single coated pressure-sensitive tapes 180° angle, 1986.

[13] American Pressure Sensitive Tape Council, Norm PSTC-7M, Holding power of pressure-sensitive tape, 1986.

[14] American Society for Testing and Materials, Norm ASTM: D3654/D3654M-02, Standard test methods for shear adhesion of pressure-sensitive tapes, 1999.

[15] C. Kiparissides, J.F. MacGregor, A.E. Hamielec, Continuous emulsion polymerization of vinyl acetate. Part I. Experimental studies, Can. J. Chem. Eng. 58 (1980) 48–55.

[16] F.J. Schork, W.H. Ray, The dynamics of the continuous emulsion polymerization of methyl methacrylate, J. Appl. Polym. Sci. 34 (1987) 1259–1276.

[17] J.B. Rawlings, W.H. Ray, Emulsion polymerization reactor stability: simplified model analysis, AIChE J. 33 (1987) 1663–1677.

[18] G. Arzamendi, C. Plessis, J.R. Leiza, J.M. Asua, Effect of the intramolecular chain transfer to polymer on PLP/SEC experiments of alkyl acrylates, Macromol. Theory Simul. 12 (2003) 315–324.

[19] P. Ilundain, L. da Cunha, R. Salazar, D. Alvarez, M.J. Barandiaran, J.M. Asua, Knowledge-based choice of the initiator type for monomer removal by postpolymerization, J. Polym. Sci. Polym. Chem. 40 (2002) 4245–4249.

[20] C. Plessis, G. Arzamendi, J.R. Leiza, H. Schoonbrood, D. Charmot, J.M. Asua, Modeling of seeded semibatch emulsion polymerization of *n*-BA, Ind. Eng. Chem. Res. 40 (2001) 3883–3894.

[21] C. Plessis, G. Arzamendi, J.M. Alberdi, M. Agnely, J.R. Leiza, J.M. Asua, Intramolecular chain transfer to polymer in the emulsion polymerization of 2-ethylhexyl acrylate, Macromolecules 34 (2001) 6138–6143.

[22] J. Wu, J.P. Tomba, A.W. Mitchell, R. Farwaha, J. Rademacher, Effect of gel content on polymer diffusion in poly(vinyl acetate-co-dibutyl maleate) latex films, Macromolecules 37 (2004) 4247–4253.

[23] D. Satas, Tailoring pressure-sensitive adhesive polymers, Adhes. Age 15 (1972) 19–23.

[24] I. Barudio, J. Guillot, G. Fevotte, Efficiency of mercaptan chain transfer agents in emulsion copolymerizations. I. Influence on kinetics and microstructure, modeling of radical desorption, J. Polym. Sci. Polym. Chem. 36 (1998) 157–168.

[25] C. Sayer, G. Arzamendi, J.M. Asua, E.L. Lima, J.C. Pinto, Dynamic optimization of semicontinuous emulsion copolymerization reactions: composition and molecular weight distribution, Comp. Chem. Eng. 25 (2001) 839–849.

[26] M.D. Gower, R.A. Shanks, The effect of chain transfer agent level on adhesive performance and peel master-curves for acrylic pressure sensitive adhesives, Macromol. Chem. Phys. 205 (2004) 2139–2150.

[27] C. Plessis, G. Arzamendi, J.R. Leiza, J.M. Alberdi, H. Schoonbrood, D. Charmot, J.M. Asua, Seeded semibatch emulsion polymerization of butyl acrylate: effect of the chain-transfer agent on the kinetics and structural properties, J. Polym. Sci. Polym. Chem. 39 (2001) 1106–1119.

[28] L. Harelle, T. Pith, G.-H. Hu, M. Lambla, Chain transfer behavior of fractionated commercial mercaptans in emulsion polymerization of styrene, J. Appl. Polym. Sci. 52 (1994) 1105–1113.

[29] J. Mendoza, J.C. de la Cal, J.M. Asua, Kinetics of the styrene emulsion polymerization using *n*-dodecyl mercaptan as chain-transfer agent, J. Polym. Sci. Polym. Chem. 38 (2000) 4490–4505.

[30] R. Jovanović, K. Ouzineb, T.F. McKenna, M.A. Dubé, Butyl acrylate/methyl methacrylate latexes: adhesive properties, Macromol. Symp. 206 (2004) 43–56.

[31] P. Ilundain, D. Alvarez, L. da Cunha, R. Salazar, M.J. Barandiaran, J.M. Asua, Modification of the microstructure of emulsion polymers, J. Polym. Sci. Polym. Chem. 41 (2003) 3744–3749.