ELSEVIER

Chemical Engineering Journal 142 (2008) 199–208

Chemical Engineering Journal

www.elsevier.com/locate/cej

Kinetic and microstructural study of the continuous emulsion polymerization of an all-acrylics formulation in the loop reactor

Iker González, Maria Paulis, José C. de la Cal, José M. Asua*

Institute for Polymer Materials, POLYMAT and Grupo de Ingeniería Química, Dpto. de Química Aplicada, University of the Basque Country, Joxe Mari Korta zentroa, 20018 Donostia-San Sebastián, Spain

Received 21 December 2007; received in revised form 1 February 2008; accepted 5 February 2008

Abstract

The suitability of a continuous loop reactor to produce all-acrylic low Tg latexes was investigated. The effect of the preemulsification level, temperature, average residence time, initiator concentration and surfactant concentration on both kinetics and polymer microstructure (gel content and molecular weight) was studied. It was shown that different polymer architectures could be obtained varying these operation variables, opening the possibility of fine tuning the polymer characteristics.

Keywords: Continuous loop reactor; Emulsion polymerization; Pressure sensitive adhesive

1. Introduction

Emulsion polymerization is used to produce waterborne dispersed polymers which are used in a large number of products including paints, adhesives, tires, paper coatings, additives for construction, textiles and impact modifiers for plastics. Commercial implementation of emulsion polymerization is mostly carried out in stirred tank reactors operated semicontinuously. Continuous stirred tank reactors, (CSTRs), are used to manufacture high tonnage emulsion polymers [1]. The use of the CSTRs provides constant quality products and easiness of on-line control. However, in these reactors the heat removal is not effective due to their low heat transfer area/volume ratio. Therefore, only small conversion increments can be achieved in a single CSTR, and a series of CSTRs has to be used to obtain high conversions. Tubular reactors are an attractive alternative because of their simple mechanical design and their large area/volume ratio, that allows an efficient heat removal. In fact they have been used to produce methyl methacrylate homopolymers and methyl methacrylate-*co*-butyl acrylate copolymers in emulsion polymerization, at solids contents up to 20% in one tubular reactor (in the case of the acrylic copolymer) and up to 40% when intermediate monomer feedings were included between two tubular reactors [2]. The poor mixing occurring in single-pass tubular reactors makes them prone to suffer phase segregation and wall fouling [3]. Static mixers (methyl methacrylate emulsion homopolymerization) [4] and internal baffles (styrene emulsion homopolymerization) [5] have been used to improve mixing and heat transfer and to avoid coagulation. However, only low solids content recipes and high Tg polymers have been produced in this type of reactors. Pulsed flow columns [6] and pulsed packed colums [7,8] provided better mixing in the reactor by the action of the externally induced pulses, although fouling may be a serious drawback in these reactors. Tubular reactors with superimposed secondary flows due to special geometries, such as the Wicker reactor [9,10] and the Taylor reactor [11,12] have also been proposed. However, the reported solids content produced in all these reactors was limited to 20% and no industrial implementation has been reported. On the contrary, the continuous loop reactor [13–17], which consists of a jacketed tubular reactor connected to the suction and discharge parts of a recycling pump (Fig. 1), which provides a high internal mixing, is used industrially for the production of vinyl acetate homopolymers and copolymers [18].

Abad et al. [19] reported that for high recycling ratios the mixing pattern of a CLR is close to the one of a CSTR. In addition for operation conditions in which the heat-removal capacity of the reactor exceeded the heat generation rate, there was no difference between the loop reactor and the CSTR in terms of conversion, particle size and number of particles, and molecular weight dis-

---

* Corresponding author. Tel.: +34 943018181; fax: +34 943017065.
E-mail address: jm.asua@ehu.es (J.M. Asua).

1385-8947/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2008.02.004

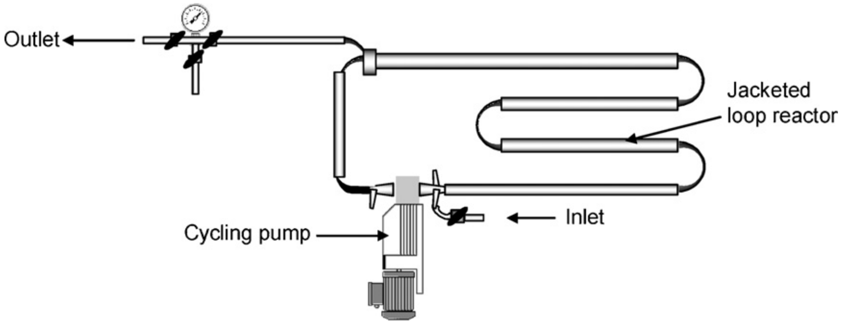

Fig. 1. Loop reactor.

tribution [20]. They also reported that under conditions in which heat generation rate was high, a thermal runaway occurred in the CSTR whereas the loop reactor was easily controlled.

Geddes [18,21] reported that a 5000 L batch tank reactor can be replaced in terms of production rate by a 50 L CLR. In addition, the cost of a CLR is about 5–10% less than that of a batch reactor plant [18,21,22]. Currently, there are about 20 commercial units in operation with an average capacity of 3000 ton/year [23] producing VAc homopolymers and copolymers. The production of all-acrylics pressure sensitive adhesives (PSAs) in the loop reactor could be a new possibility that has not been reported in the literature yet.

In this article, the suitability of the loop reactor to produce all-acrylics latex adhesives at high solids content is explored. The critical requirement for the formulations is that the system should remain stable under shear during polymerization (due to the presence of the recycling pump). The existance of mass transfer limitations and the effect of temperature, residence time, and initiator and surfactant concentrations on the monomer conversion, number of particles in the reactor, total gel content and molecular weight was studied.

2. Experimental section

2.1. Materials

Technical grade monomers were used: 2ethyl hexyl acrylate (2EHA) and methyl methacrylate (MMA) were both supplied by Quimidroga. Acrylic acid (AA) was supplied by Fluka. Dowfax 2A1 (alkyldiphenyloxide disulfonate, Dow Chemical) was used as anionic surfactant and sodium bicarbonate (Fluka) was used as buffer. A redox initiator system was used with $(NH_4)_2S_2O_8$ (APS, Fluka) as oxidant and $Na_2S_2O_5$ (SBS, Fluka) as reductant. Double deionized water was used in all the reactions.

2.2. Characterization

The total monomer conversion (defined as polymer weight divided by the weight of monomer plus polymer in the reactor) was measured by gravimetry and gas chromatography (Shimadzu GC 14-A). The mean droplet and particle diameters were measured by dynamic light scattering (Coulter N4 Plus). The number of particles (Np) in the system was calculated from the monomer conversion and the particle diameter. Particle size distributions were measured by capillary hydrodynamic fractionation (CHDF 2000, Matec). A modified Cohen Addad's method [24] was used to determine the gel content of the polymer. The method consisted in an extraction with THF at 65 °C in a 1 L glass reactor, for 8 h. In order to obtain the average molecular weights of the soluble polymer, soxhlet gel extractions of samples taken during the steady state of the reactions were carried out. Tetrahydrofurane (THF) was used as solvent and the extractions were carried out during 24 h. Static Light Scattering (Zetasizer Nano, Malvern) was used to determine the weight average molecular weight. The stability of the preemulsions was determined with a Turbiscan Lab^{expert} apparatus. In this equipment, the sample contained in a glass cylindrical cell was vertically scanned with a laser light and the backscattered light, which is sensitive to the droplet size and dispersed phase concentration, was recorded.

2.3. Polymerization in the loop reactor

The loop reactor used (Fig. 1) consisted of a stainless steal tube (AISI 310) of 10 mm internal diameter and 6 m long ($V = 0.52$ L, $A/V = 3.65$ m^{-1}), connected to the suction and discharge parts of a lobe rotary pump (HY-Line by Jabs Co., internal volume of the pump = 0.125 L). Most of the straight parts of the reactor were jacketed with a tube of 3 cm in diameter, for temperature control. The monomers and the aqueous solution of initiator and surfactants were stored in tanks connected to the feeding pumps through three-way valves placed at the bottom of the storage tanks. These tanks were also equipped with a nitrogen purge. The feed flow rate of the monomers and the aqueous phase (surfactant, buffer and water) was controlled by Kflow PICO 2 (ABB) mass flow controllers. The feed flow rate of the initiator solution was gravimetrically controlled using a Flow Pack (Mettler) controller. The feeds were pumped using three membrane pumps (Prominent Gamma 4 and Gamma 5), that were controlled by the Kflow controllers. The feeds were premixed before entering the reactor, in a continuous magnetically stirred tank followed by a continuous sonication cell (Branson 450W). Sonication is exothermic and a thermostatic bath was used to remove the generated heat. All the reactions were started-up with the loop reactor filled with an aqueous solution of surfactant, buffer and SBS.

Table 1
All-acrylic adhesive formulation for the loop reactor

Component	Stream 1 (wt%)	Stream 2 (wt%)	Stream 3 (wt%)
MMA	7		
2EHA	92		
AA	1		
Dowfax 2A1 (45 wt% act.)		3.13	
KPS			3.7
SBS		0.24	
Buffer		0.29	
Water		96.34	96.3
Feeding flow (g/min)	16.5	23.5	1.84

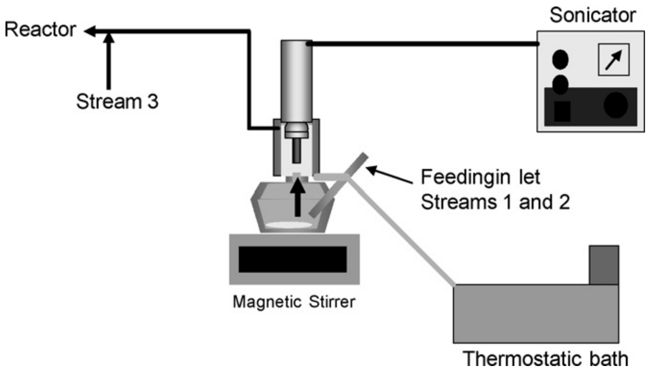

Fig. 2. Premixing system.

3. Mass transfer limitations

The major component of the formulation (2EHA) is a rather water insoluble monomer, whose mass transfer rate to the polymerization loci (polymer particles) might be slow. In these systems, the rate determining step for mass transfer is the diffusion from the monomer droplets to the aqueous phase [25]. Therefore, in order to increase the mass transfer rate, the size of the monomer droplets was reduced by sonicating the coarse emulsion prior the reactor entrance. Table 1 presents the formulation used in these reactions.

Two reactions were carried out (Mixed-1000-emulsion and Mixed-700-emulsion) in which reactants were only passed through a magnetically stirred cell using different stirring speeds. Additionally, a sonicated emulsion was fed, in which the coarse emulsion produced in the stirred cell was passed through a sonication cell prior entering into the reactor (Fig. 2). Table 2 shows that sonication yielded smaller droplets.

Polymerizations were carried out at 70 °C with a mean residence time (τ) of 15 min and a recycling ratio of 121. With this recycling ratio the residence time distribution of the continuous loop reactor was that of a well mixed CSTR [19]. Fig. 3 presents the evolution of the total number of particles in the reactor (Np) as a function of normalized reaction time (t/τ).

Table 2
Premixing conditions of the different reactions

Reaction	Sonication (J/g)	Magnetic stirring (rpm)	Droplet diameter (nm)
Mixed-700-emulsion	0	700	299
Mixed-1000-emulsion	0	1000	259
Sonicated emulsion	0.17	700	156

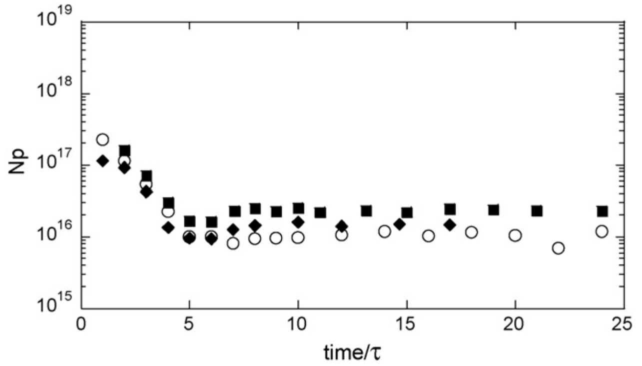

Fig. 3. Effect of premixing conditions on Np (total number of particles in the reactor). (○) Mixed emulsion (700 rpm); (◆) mixed emulsion (1000 rpm); (■) sonicated emulsion.

It can be seen that the number of particles increased with the premixing intensity. There may be two factors contributing to this increase. First, a more efficient use of the radicals produced by the initiator. The redox initiator system generated a high radical flux. The sulphate radical anions generated were too hydrophilic to be able to enter into the organic phases (micelles, monomer droplets) [26–28]. Consequently, they had to react first with the monomer dissolved in the aqueous phase, forming oligoradicals able to enter into the micelles once they were hydrophobic enough. The efficiency of this process depends on the availability of monomer in the aqueous phase, which in turn depends on the mass transfer from monomer droplets. Therefore, improving this mass transfer by increasing the intensity of mixing led to a higher nucleation rate.

A second factor could be the contribution of droplet nucleation. In order to be nucleated the droplets should be stable during a certain period of time. Fig. 4 presents a droplet stability test of the sonicated emulsion with the formulation presented in Table 1.

In this plot, the reduction of the backscattering intensity is an indication of the increasing droplet size. It can be seen that the sonicated emulsion was rather stable for about 4 min and even at 10 min it did not show much creaming. This result indicates that monomer droplets could maintain their identity in the reactor for a significant fraction of their residence time

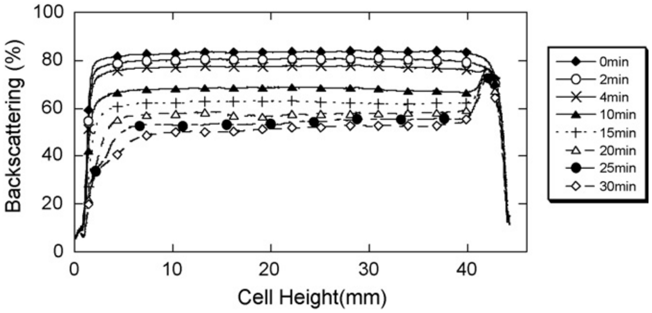

Fig. 4. Stability test of the sonicated emulsion.

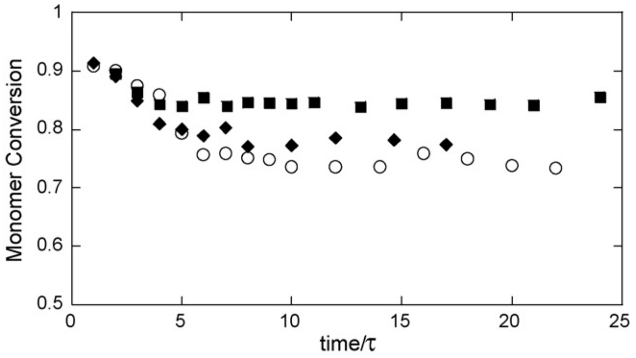

Fig. 5. Effect of premixing conditions on monomer conversion. (○) Mixed emulsion (700 rpm); (◆) mixed emulsion (1000 rpm); (■) sonicated emulsion.

($\tau = 15$ min), and hence the contribution of droplet nucleation could be significant. It is important pointing out that in the presence of particles, diffusion degradation may be faster. On the other hand, mixed emulsions separated as soon as the mechanical stirring was stopped, eliminating any probability of droplet nucleation in that case.

Fig. 5 shows that monomer conversion increased with the intensity of premixing. This increment has been attributed to both the higher number of particles and the faster monomer mass transfer. This faster mass transfer can have two effects. On one hand, it may accelerate the monomer mass transfer to the polymer loci (polymer particles) and on the other hand it may allow a more efficient use of the initiator system. The data of the gel content, which will be shown next, indicate that this second effect was likely more important.

Emulsion homopolymerization or copolymerization of 2EHA yields a polymer containing a significant gel fraction. Fig. 6 presents the effect of the premixing procedure on the gel content, measured with replicated samples taken during the steady state of the reaction. Gel is formed by intermolecular chain transfer to polymer followed by termination by combination. These two processes are common in polymerization of acrylic monomers [29,30]. Intermolecular chain transfer to polymer increases with polymer concentration and hence with conversion. Fig. 6 shows that gel content was higher for the sonicated emulsion. This supports the hypothesis that the higher number of particles and the more efficient use of the initiator were the reason for a higher conversion when the intensity of premixing increased. If the lower conversion achieved with mixed emulsions were due to mass transfer limitations, the concentration of monomer in the polymer particles would be relatively low, which would lead to a higher rate of intermolecular chain transfer to polymer, namely to a higher amount of gel.

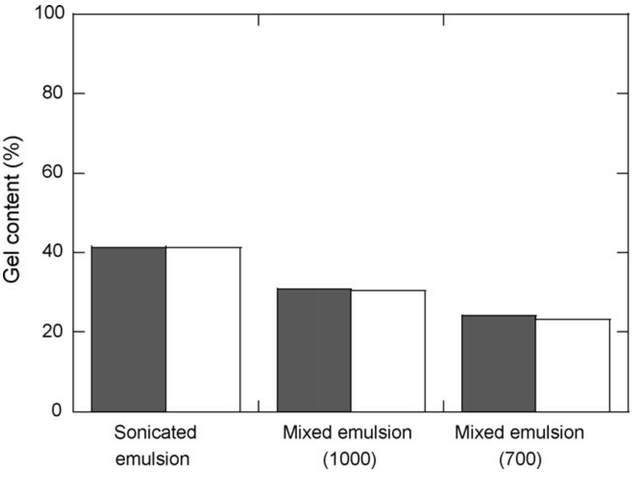

Fig. 6. Effect of the premixing conditions on the gel content.

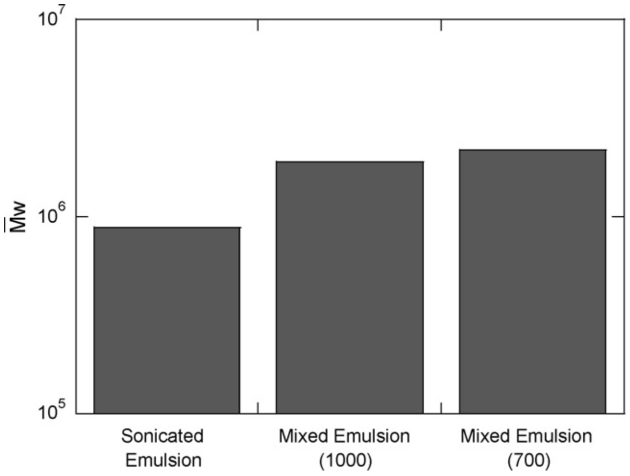

Fig. 7. Effect of the premixing conditions on sol molecular weight.

Fig. 7 presents the effect of the premixing conditions on the sol molecular weight of samples taken during the steady state of the reaction. It can be observed, that the sol molecular weight increased when the supplied energy decreased. These results were closely related to the evolution of gel in Fig. 6. In this system, gel is formed by intermolecular chain transfer to polymer followed by the termination by combination. As intermolecular chain transfer to polymer is proportional to the polymer length, the longer chains are preferently incorporated into the gel leading to a decrease of the sol molecular weight.

4. Effect of the temperature

In order to study the effect of the reaction temperature in the loop reactor, three reactions were carried out with the formulation presented in Table 1, a residence time of 15 min, at 60, 70 and 80 °C and sonicating the coarse emulsion. Fig. 8 presents the effect of the temperature on the number of particles as a function of the normalized reaction time (t/τ). It can be seen that temperature did not affect nucleation.

In addition, Fig. 9 shows the PSD (measured by CHDF) of the reactions carried out at 60, 70 and 80 °C. The shape of the PSDs suggests a continuous nucleation process. Furthermore, the temperature did not affect the PSD during the steady state. A possible reason for the lack of sensitivity of Np was that the initiator system was a redox pair and in such a case, the radical generation rate is very fast and radical production rate is determined by the initiator feed rate, and hence not influenced by the temperature.

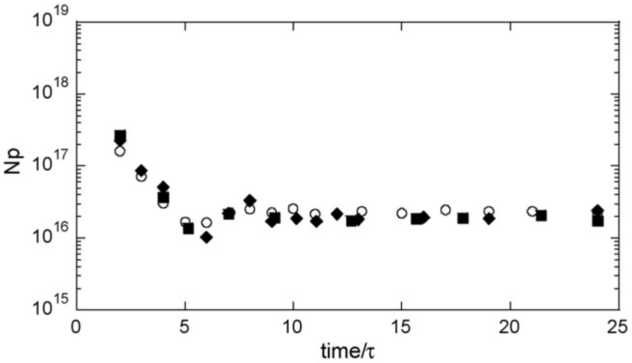

Fig. 8. Effect of temperature on Np (♦) 60 °C; (○); 70 °C; (■) 80 °C.

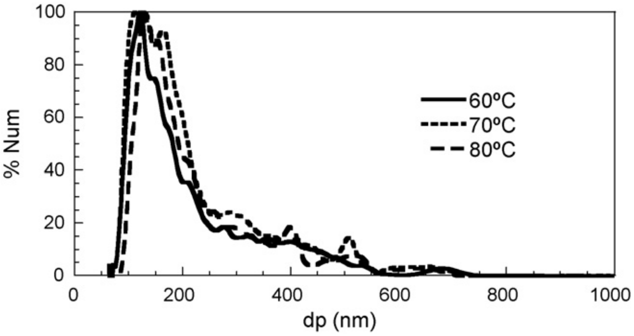

Fig. 9. Particle size distributions in the steady state for reactions carried out at different temperatures.

Fig. 10 shows that an increase in the reaction temperature caused only a slight increase in monomer conversion. This increase was likely due to the effect of temperature on the propagation rate constant. In this context, it is worth pointing out that the effect of temperature on the apparent k_p in the polymerization of acrylic monomers is reduced by the increase in the formation of low-reactive tertiary radicals by chain transfer to polymer, because the activation energy of this process is higher than that of the propagation [31]. In all the cases, gas chromatographs showed that the conversion of MMA was almost complete.

Fig. 11 presents the gel content at the steady state (two different measurements for each sample) of the reactions carried out at different temperatures. It can be observed that an increase in the reaction temperature led to an increase in the gel content. This behaviour can be explained taking into account that the activation energy of the intermolecular chain transfer to polymer (that followed by termination by combination generated the insoluble polymer fraction) is higher than the activation energy of the propagation. Therefore, intermolecular chain transfer process is favoured at higher temperatures, leading to higher gel contents [31].

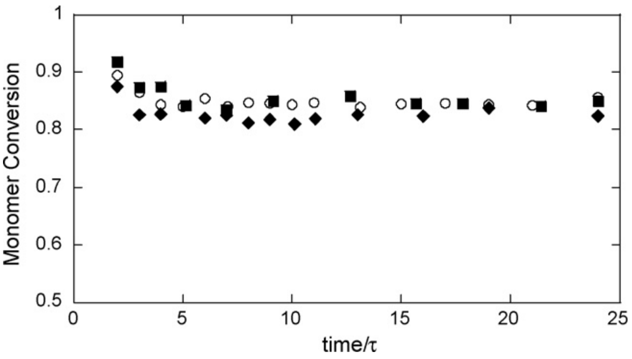

Fig. 10. Effect of temperature on monomer conversion (♦) 60 °C; (○); 70 °C; (■) 80 °C.

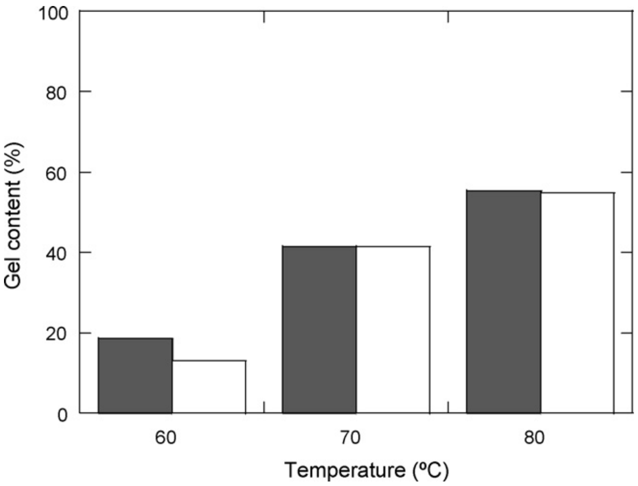

Fig. 11. Effect of the reaction temperature on gel content.

Fig. 12 shows that the molecular weight of the soluble part slightly decreased with the reaction temperature. This was due to the preferent incorporation of the long chains to the gel. In free radical polymerization using thermal initiators, an increase in the reactor temperature leads to a reduction of the kinetic length mostly because radical formation substantially increases with temperature (the activation energy of initiator decomposition rate constant is very high). However, when using redox systems, above a certain temperature, the rate of radical formation does not increase (simply because of the complete reaction of redox system) and the effect of temperature on the kinetic length is only function of the relative values of the activation energies of propagation, termination and chain transfer, which are not that different.

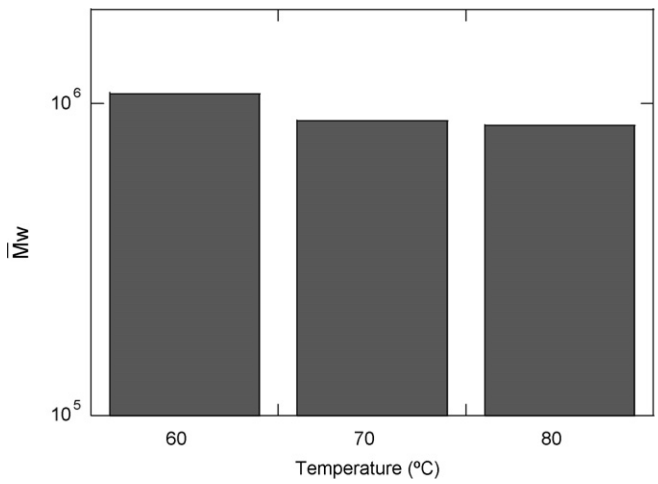

Fig. 12. Effect of the reaction temperature on sol molecular weight.

Table 3
Feeding flow rates for reactions with different residence times

Residence time (min)	Stream 1 (g/min)	Stream 2 (g/min)	Stream 3 (g/min)
10	24.8	35.22	2.76
15	16.5	23.5	1.84
20	12.4	17.6	1.38

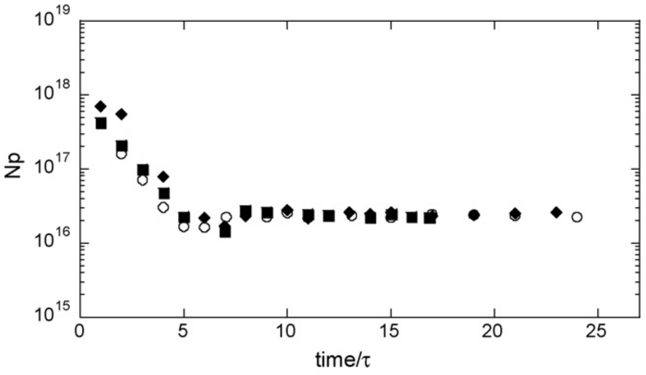

Fig. 13. Effect of the average residence time on Np (◆) $\tau = 10$ min; (○) $\tau = 15$ min; (■) $\tau = 20$ min.

5. Effect of the residence time

Reactions using the mean residence times given in Table 3 were carried out with the formulation presented in Table 1 at 70 °C. The sonication parameters were adapted to each case in order to supply to the preemulsion the same energy per unit volume. The recycling ratio was kept constant in all experiments ($R = 121$) by adjusting the flow rate of the recycling pump in each reaction.

Fig. 13 shows that nucleation was not affected by the residence time. Fig. 14 shows that PSD was practically the same for all the residence times. The shape of the PSDs suggests again a continuous nucleation process.

Fig. 15 shows that monomer conversion slightly increased with the average residence time. Almost no MMA was detected by GC. This small increase in monomer conversion was due to the fact that in the free radical polymerization of acrylic monomers, $k_{\mathrm{p\ apparent}}$ substantially decreases when the monomer concentration decreases [32]. Therefore, it is very difficult to increase the conversion of the monomer above a certain value. Another factor is that for a redox system, the concentration of radicals in the reactor decreased as the residence time increased.

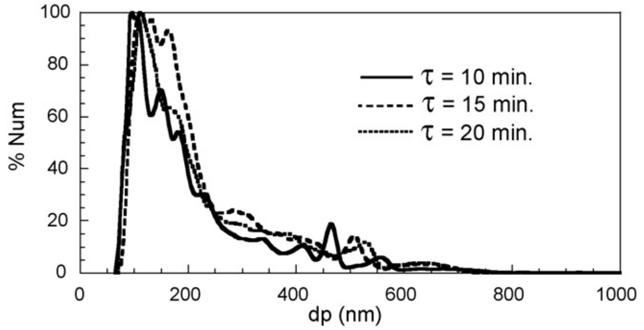

Fig. 14. Particle size distributions in the steady state for reactions with 10, 15 and 20 min of residence time.

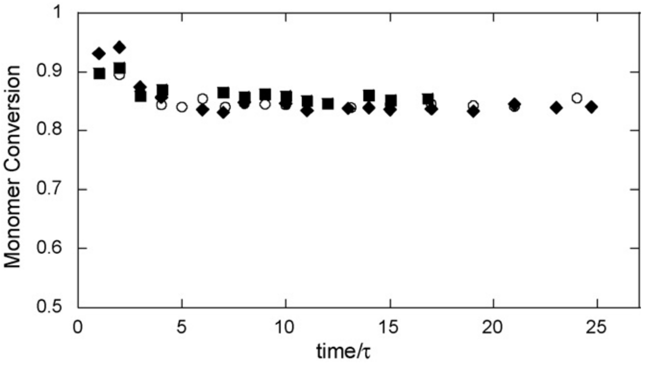

Fig. 15. Effect of the average residence time on monomer conversion (◆) $\tau = 10$ min; (○) $\tau = 15$ min; (■) $\tau = 20$ min.

On the other hand, Fig. 16 shows that there was only a modest increase in the gel content when the residence time was increased. This may partially be due to the slight increase in monomer conversion observed in Fig. 15, which favoured an increase in the probability of transfer to polymer. Another factor is that as the residence time increased, the probability of a polymer chain suffering chain transfer to polymer increased, and hence gel formation was more likely.

Fig. 17 presents the effect of the residence time on the sol molecular weight. It can be observed that the molecular weight slightly decreased when the residence time increased. This is related to the increase in the gel content, which preferentially incorporates long chains.

6. Effect of the initiator concentration

Reactions with 0.75 wt% (Table 1), 1.25 wt% (Table 4) and 1.5 wt% of initiator (KPS + SBS) (based on the total amount of monomers) were carried out. All the reactions were carried out at 70 °C, sonicating the coarse emulsion, with 2 wt% of surfactant (based on the total amount of monomers) and with a residence time of 15 min.

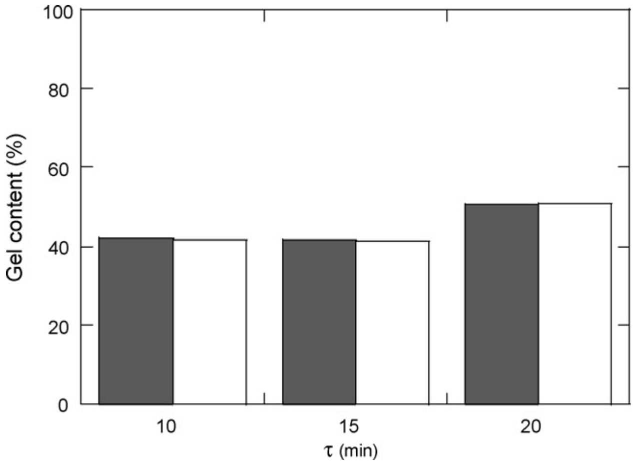

Fig. 16. Effect of the residence time on gel content.

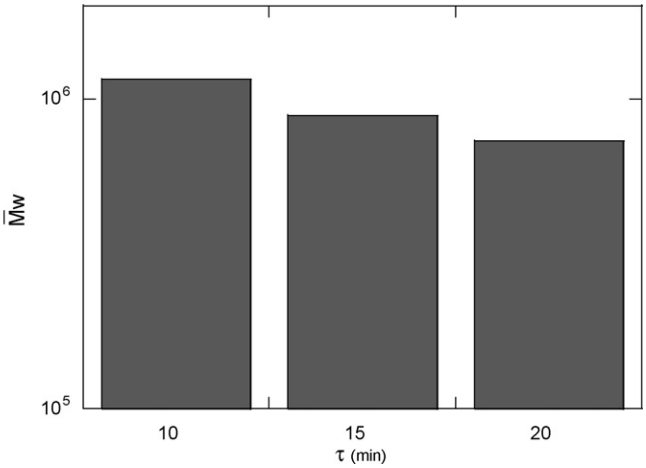

Fig. 17. Effect of the residence time on the sol molecular weight.

Table 4
Formulation with 1.25 wt% of initiator

Component	Stream 1 (wt%)	Stream 2 (wt%)	Stream 3 (wt%)
MMA	7		
2EHA	92		
AA	1		
Dowfax 2A1 (45 wt% act.)		3.28	
KPS			3.67
SBS		0.42	
Buffer		0.4	
Water		95.9	96.33
Feeding flow (g/min)	16.5	22.6	3.0

Figs. 18 and 19 present the effect of the initiator concentration on both monomer conversion and number of polymer particles in the reactor. It can be seen that an increase in the initiator concentration from 0.75 to 1.25 wt% led to an increase in monomer conversion, but there was no effect on the number of polymer particles. In the case of using 1.5 wt% of initiator, the reaction had to be stopped after seven residence times because the feed to the reactor became very viscous creating problems in the flow rate control. The reason for such a viscosity increase could be the nucleation of small droplets in the continuous sonication cell. It has been reported that the polymerization can be initiated by a reaction between the sodium bisulfite and the acrylic monomers [33]. This process could be enhanced by the energy supplied with the sonication system.

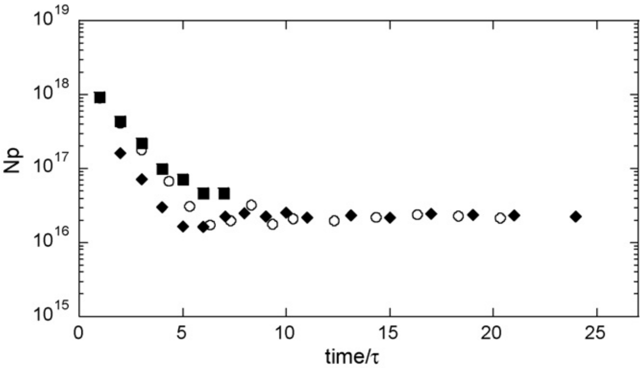

Fig. 18. Effect of initiator concentration on Np (♦) 0.75 wt%; (○); 1.25 wt%; (■) 1.5 wt%.

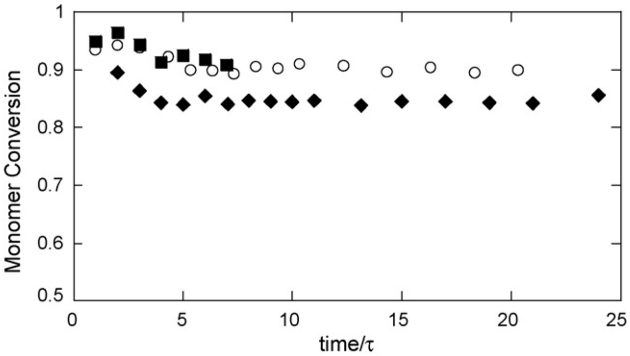

Fig. 19. Effect of initiator concentration on monomer conversion (♦) 0.75 wt%; (○); 1.25 wt%; (■) 1.5 wt%.

It was checked if polymerization occurred in the continuous sonication cell with 0.68 wt% of the reductant component of the initiator system (SBS) (corresponding to a total initiator concentration of 1.5 wt%) in the feed at varying the energy levels. Fig. 20 shows that a substantial monomer conversion was reached in the sonication cell using the energy employed in the reaction presented above (0.17 J/g).

It has to be pointed out that 0.57 wt% SBS (corresponding to a total initiator concentration of 1.25 wt%) led to negligible monomer conversions at the sonication energy level given in the process (0.17 J/g).

Fig. 21 shows that the gel content was not affected by the initiator concentration. This result could be due to two opposite effects. On one hand, the increase in conversion favoured intermolecular chain transfer to polymer. On the other hand, this increase in initiator concentration led to shorter average kinetic length. These counteracting effects could explain the insensitivity of the gel content to the initiator concentration.

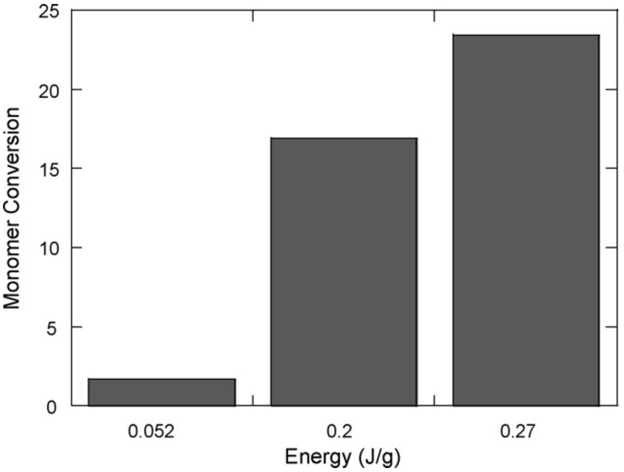

Fig. 20. Effect of the energy supplied in the sonication on the monomer conversion leaving the continuous sonication cell.

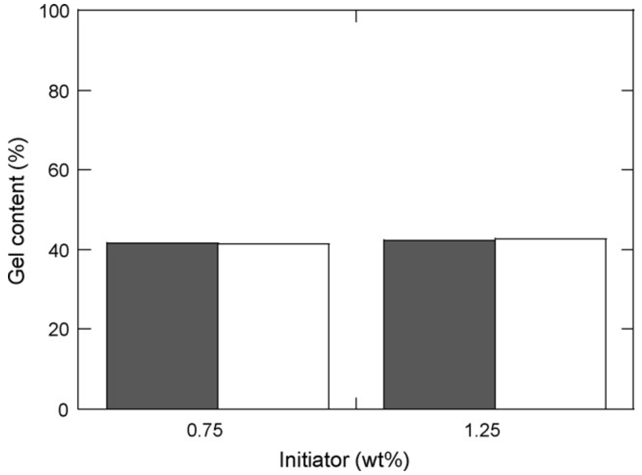

Fig. 21. Effect of initiator concentration on gel content.

Fig. 22 shows that the initiator concentration did not significantly affect the sol molecular weight. The counteracting effects of the higher conversion (higher intermolecular chain transfer to polymer) and the shorter kinetic chain length may be the reason of this insensitivity.

7. Effect of the surfactant concentration

Reactions using 1, 1.5 and 2 wt% of surfactant (based on the total amount of monomers) were carried out. The compositions of the different aqueous phases are presented in Table 5. All these reactions were carried out at 70 °C, sonicating the coarse emulsion and with a residence time of 15 min.

Fig. 23 shows that Np increased with surfactant concentration. The concentration of surfactant also affected the particle size distribution. Fig. 24 shows that with the lowest surfactant concentration (1 wt%), a low frequency intermittent nucleation occurred. This is in contrast with the results presented with the highest surfactant concentration (2 wt%) where an almost continuous nucleation was evident.

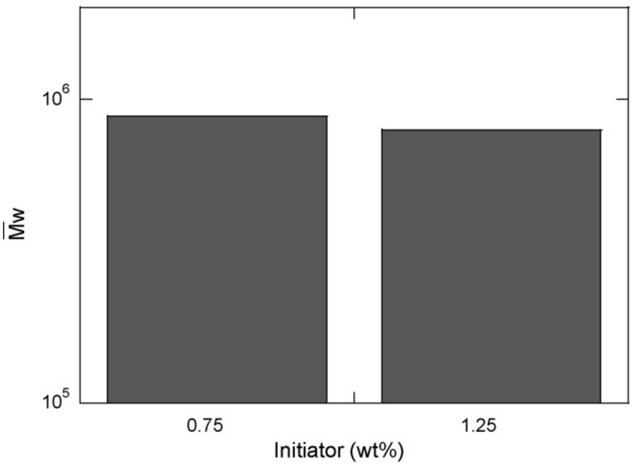

Fig. 22. Effect of initiator concentration on the sol molecular weight.

Table 5
Aqueous phase formulation for the different reactions carried out with different surfactant percentages (Stream 2)

Component	Surfactant (1 wt%)	Surfactant (1.5 wt%)	Surfactant (2 wt%)
Dowfax 2A1 (45 wt% act)	1.58	2.36	3.13
SBS	0.24	0.24	0.24
Buffer	0.29	0.29	0.29
Water	97.89	97.11	96.34

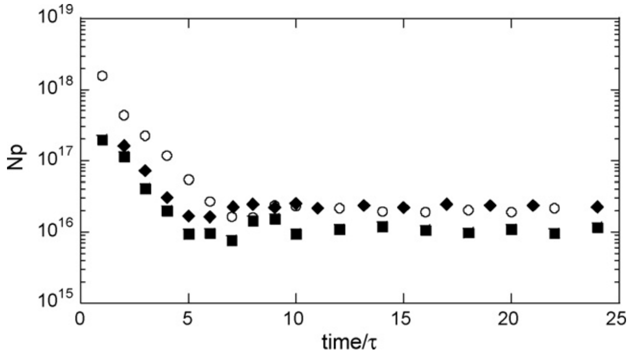

Fig. 23. Effect of surfactant concentration on Np (◆) 2 wt%; (○) 1.5 wt%; (■) 1 wt%.

Intermittent nucleation is characteristic of micellar nucleation in well mixed continuous reactors [34–36]. Particles are initially produced by micellar nucleation. As these particles grow, their area increases so that the total area of the particles exceeds the area that can be covered by the surfactant at maximum packing (i.e., in the presence of micelles). Therefore, most of the surfactant is absorbed on the particles, and particle nucleation ceases. Nucleation does not restart until enough particles

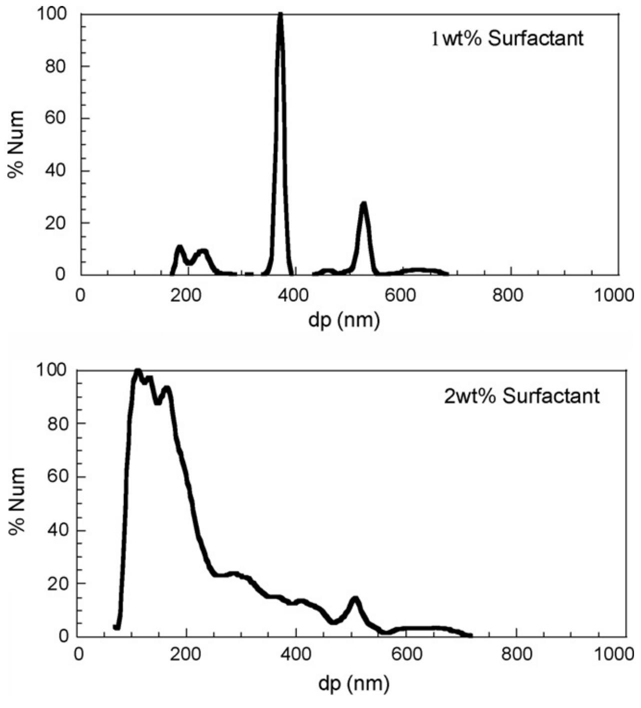

Fig. 24. Particle size distribution at the steady state in reactions carried out with 1 and 2 wt% of surfactant.

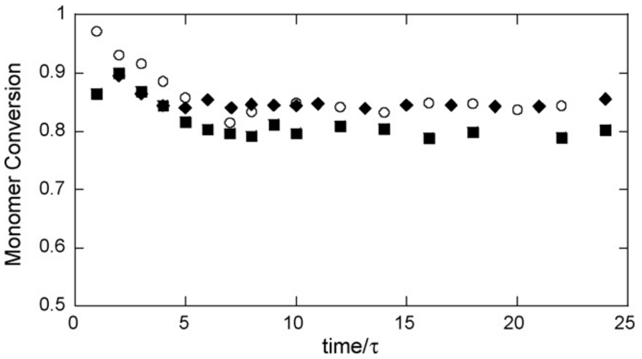

Fig. 25. Effect of surfactant concentration on monomer conversion (♦) 2 wt%; (○) 1.5 wt%; (■) 1 wt%.

leave the reactor and the total area of the particles is smaller than the area that can be covered by the surfactant at maximum packing. At this moment, micelles are formed again and a new nucleation occurs. The frequency of intermittent nucleations increases with the surfactant concentration.

Fig. 25 shows that monomer conversion increased with surfactant concentration following the trend in Np. In addition, gas chromatographs showed that the residual monomer was mostly the least reactive monomer (2EHA).

Fig. 26 shows that the gel fraction decreased as the concentration of the surfactant increased. This is interesting because monomer conversion increased with increasing surfactant concentration and hence an increase of the gel content would be expected due to the higher rate of intermolecular chain transfer to polymer. However, as surfactant concentration increased, Np increased, and therefore the average number of radicals per particle ($\bar{n}$) decreased, reducing the rate of bimolecular termination between large macromolecules, which would reduce the rate of gel formation.

Fig. 27 shows that as surfactant concentration increased the sol molecular weight decreased. This is an unexpected result, as the decrease of the gel content when the emulsifier concentration increased should be accompanied by an increase of sol molecular weight, but the opposite trend was observed. The reduction of bimolecular termination can be a reason for this result.

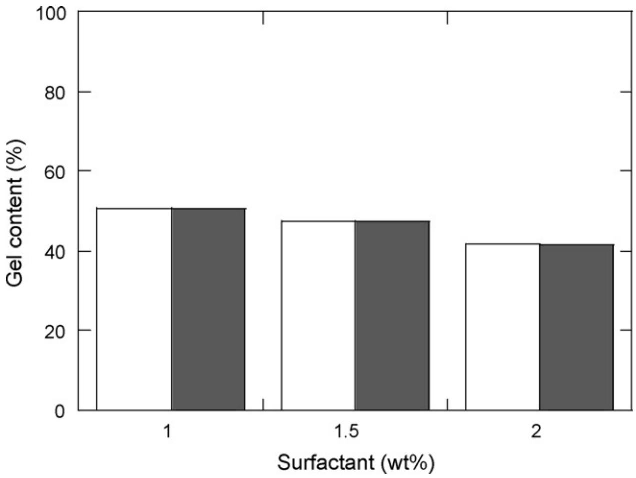

Fig. 26. Effect of surfactant concentration on gel content.

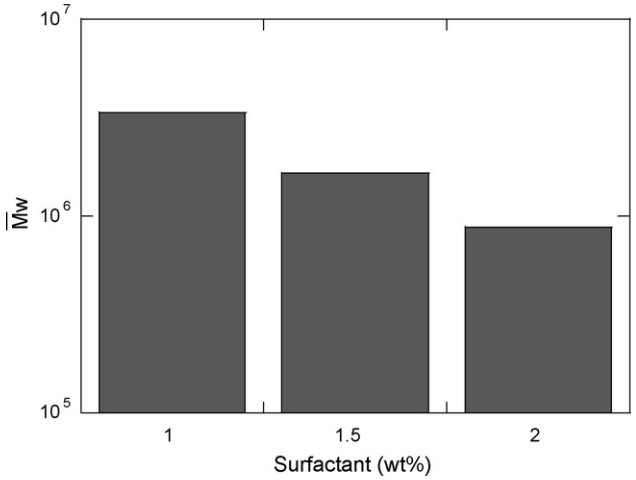

Fig. 27. Effect of surfactant concentration on sol molecular weight.

8. Conclusions

The suitability of the loop reactor to produce all-acrylic latexes (2EHA/MMA/AA 92/7/1 wt/wt) for pressure sensitive adhesives was confirmed. Latexes with 40 wt% solids content with no coagulum were obtained, for a low Tg copolymer under different operation conditions.

The reduction of the droplet size of the premixed feed led to an increase in the number of particles and the monomer conversion. This behaviour was mainly due to a more efficient use of the initiator as a result of an improvement in the monomer mass transfer achieved by reducing the size of the monomer droplets in the feed. The effect of the premixing conditions on the sol molecular weight and gel content seems to confirm this idea. The polymerization temperature did not affect nucleation and only slightly monomer conversion, but gel content increased due to the higher activation energy of the intermolecular chain transfer to polymer compared with propagation. The effect of the average residence time on the number of particles, monomer conversion, sol molecular weight and gel content was almost negligible for the values studied in this paper. The decrease of the apparent propagation constant for lower monomer concentrations can be the reason for this insensitivity. Monomer conversion significantly increased with initiator concentration, but the number of polymer particles was not affected. Neither gel content nor sol molecular weight were affected by this variable, probably due to the counteracting effects of the higher conversion (greater intermolecular chain transfer to polymer) and shorter kinetic chain length. The number of polymer particles increased with the surfactant concentration. Intermittent nucleations were observed at low surfactant concentrations, whereas an almost continuous nucleation occurred at higher surfactant concentrations. Gel content decreased with surfactant level, as a consequence of a lower number of radicals per particle.

Acknowledgements

I. González thanks the grant from the Universidad del País Vasco/Euskal Herriko Unibertsitatea. The financial support by the Diputación Foral de Gipuzkoa and Ministerio de Educación y Ciencia (CTQ2006-03412/PPQ) is acknowledged.

References

[1] G.W. Poehlin, in: J.M. Asua (Ed.), Polymeric Dispersions: Principles and Applications, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1997.

[2] K. Ouzineb, C. Graillat, T. McKenna, J. Appl. Polym. Sci. 91 (2004) 2195.

[3] D.A. Paquet, W. H. AIChE J. 40 (1994) 73.

[4] S. Fan, J.H.G. Steinke, E. Alpay, Ind. Eng. Chem. Res. 44 (2005) 5483.

[5] F.L. Mendoza Marín, L.M. Ferrareso Lona, M.R. Wolf Maciel, R. Maciel Filho, J. Appl. Polym. Sci. 102 (2006) 6037.

[6] M.J. Mayer, J. Meuldijk, D. Thoenes, Chem. Eng. Sci. 49 (1994) 4971.

[7] C.A. Scholtens, J. Meuldijk, A.A.H. Drinkenburg, Chem. Eng. Sci. 56 (2001) 955.

[8] A.C.S.M. Carvalho, D. Chicoma, C. Sayer, R. Giudici, Macromol. Symp. 243 (2006) 147.

[9] M. Apostel, W. Pauer, H.U. Moritz, J. Kremeskotter, K.D. Hungenberg, Chimia 55 (2001) 229.

[10] C. Heibel, J. Kremeskötter, S. Funkhauser, W. Hübinger, WO 99/44737 (1999).

[11] X. Wei, H. Tahahashi, S. Sato, M. Nomura, J. Appl. Polym. Sci. 80 (2001) 1931.

[12] W. Pauer, H.U. Moritz, Macromol. Symp. 243 (2006) 299.

[13] K. Geddes, Polym. Paint Colour J. 176 (1983) 494–500.

[14] K. Geddes, Br. Polym. J. 21 (1989) 433.

[15] D.C. Adams, H. Jones, K. Geddes, WO 00/07717 (2000).

[16] D.C. Adams, WO 01/34293 (2001).

[17] D.C. Adams, WO 2007/031478 (2007).

[18] K. Geddes, Chem. Ind. 21 (1983) 223.

[19] C. Abad, J.C. de la Cal, J.M. Asua, Chem. Eng. Sci. 49 (1994) 5025.

[20] C. Abad, J.C. de la Cal, J.M. Asua, J. Appl. Polym. Sci. 56 (1995) 419.

[21] K. Geddes, Polym. Paint Colour J. 176 (1985) 494.

[22] K. Geddes, JOCCA 76 (1993) 330.

[23] D. Adams, Akzo Nobel, personal communication, 2007.

[24] J.P. Cohen-Addad, C. Bojonuk, V. Granier, Macromolecules 27 (1994) 5032.

[25] D. Urban, l. Egan, in: D. Urban, K. Takamura (Eds.), Polymer Dispersions and their Industrial Applications, Willey–VCH, Weinheim, Germany, 2002.

[26] M. Goicoechea, M.J. Barandiaran, J.M. Asua, Macromolecules 39 (2006) 5165.

[27] F.K. Hansen, J. Ugelstad, J. Polym. Sci. Polym. Chem. Ed. 16 (1978) 1979.

[28] F. Coen, R.A. Lyons, R.G. Gilbert, Macromolecules 29 (1996) 5128.

[29] C. Plessis, G. Arzamendi, J.M. Alberdi, M. Angely, J.R. Leiza, J.M. Asua, Macromolecules 34 (2001) 6138.

[30] C. Plessis, G. Arzamendi, J.R. Leiza, M.A.S. Schoonbrood, D. Charmot, J.M. Asua, Ind. Eng. Chem. Res. 41 (2001) 3883.

[31] G. Arzamendi, C. Plessis, J.R. Leiza, J.M. Asua, Macromol. Theor. Simul. 12 (2003) 315.

[32] I. Gonzalez, J.R. Leiza, J.M. Asua, Macromolecules 39 (2006) 5015.

[33] R. Mukherjee, P. Gosh, S.C. Chadhe, S.R. Palit, Makromol. Chem. 80 (1964) 208.

[34] F.J. Schork, W.H. Ray, J. Appl. Polym. Sci. 34 (1987) 1259.

[35] C. Kiparissides, J.F. MacGregor, A.E. Hamielec, Can. J. Chem. Eng. 58 (1980) 48.

[36] P.H.H. Araujo, C. Abad, J.C. de la Cal, J.C. Pinto, J.M. Asua, Polym. React. Eng. 7 (1999) 303.