

The role of methyl methacrylate on branching and gel formation in the emulsion copolymerization of BA/MMA

Iñigo González, José M. Asua, José R. Leiza*

Institute for Polymer Materials, POLYMAT and Grupo de Ingeniería Química, Dpto. de Química Aplicada, Facultad de Ciencias Químicas, The University of the Basque Country, P.O. Box 1072, 20080 Donostia-San Sebastián, Spain

Received 14 December 2006; received in revised form 21 February 2007; accepted 6 March 2007

Available online 12 March 2007

Abstract

The effect of the monomer ratio on the microstructure of BA/MMA emulsion copolymers was investigated. Monomer ratios spanned from pure BA used for adhesives to 50/50 wt/wt BA/MMA copolymers used for coatings. The gel content varied from 55% for pure BA to nil for the 50/50 copolymer. The branching level was reduced from 2.6% for pure BA to 0.3% for a 75/25 BA/MMA copolymer. The mechanisms responsible for the reduction of gel content can be found in the lower reactivity of the MMA terminated chains for hydrogen abstraction, the absence of abstractable hydrogens in the MMA units and the fact that MMA radicals terminate predominantly by disproportionation. The reduction of the level of branches is mainly due to the lower reactivity of MMA for intramolecular transfer and the lower instantaneous conversions that favored propagation over backbiting.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Emulsion polymerization; Backbiting; Chain transfer to polymer gel content

1. Introduction

Butyl acrylate/methyl methacrylate, BA/MMA, emulsion copolymers are very versatile materials extensively used as adhesives (BA homopolymers and BA-rich copolymers) and coatings (BA/MMA 50/50 wt/wt copolymers). In spite of their commercial importance, only a few literature reports dealing with the microstructural properties of BA/MMA emulsion copolymers have been published [1–3]. In the semibatch emulsion polymerization of BA/MMA (50/50 wt/wt), Sayer et al. [1] studied the effect of the CTA (dodecanethiol) on the kinetics and the microstructural properties of the polymer. It was reported that the addition of a CTA did not affect the polymerization kinetics, but the molecular weights strongly decreased and gel formation was avoided for CTA concentrations above 1 wt%. In addition, they observed that higher values of gel and lower molecular weights were obtained

in the starved process in comparison with the semi-starved processes. In the semicontinuous emulsion polymerization of BA/MMA with a comonomer composition of 50/50 and reaction temperatures between 75 and 85 °C, Parouti et al. [2] found that the sol molecular weight (the molecular weight of the soluble fraction of the polymer) increased as the initiator concentration and/or temperature decreased. The final gel content increased with increasing initiator concentration and decreasing temperature. Elizalde et al. [3] studied the effect of the monomer composition (BA/MMA: 50/50, 70/30 and 90/10) on the kinetics and microstructural properties of the copolymer (average sol molecular weights and gel content) produced in the seeded semibatch emulsion copolymerization carried out at 75 °C. They found that the increase of MMA strongly reduced the gel content because of the decrease in the chain transfer to polymer processes.

Britton et al. [4] measured by ¹³C NMR the level of branches in BA/MMA/AA copolymerizations (90/5/5 and 85/10/5, mol/mol) obtained in semibatch emulsion polymerization. They reported that the presence of MMA led to a substantial decrease of the level of branches (quaternary carbons

* Corresponding author. Tel.: +34 943015329; fax: +34 943015270.

E-mail address: jrleiza@ehu.es (J.R. Leiza).

in the polymer backbone). The results were interpreted in terms of the lower reactivity of the MMA radicals as compared to BA and AA radicals. However, backbiting, which is the main mechanism for formation of branching points [5–7] was not considered and gel measurements were not reported.

In this work, the effect of the monomer ratio (from pure BA used for adhesives to 50/50 wt/wt BA/MMA used for coatings) on the microstructure (gel and branching) of polymers produced by semicontinuous emulsion polymerization was investigated. Both properties strongly influence the mechanical properties of coatings and adhesives and therefore understanding the effect of comonomer ratio on these properties is important in order to tailor made the required application properties.

2. Experimental section

2.1. Materials

BA and MMA (Quimidroga) and MAA (Aldrich) were used as received. Sodium lauryl sulfate (Aldrich) was used as emulsifier for the seed preparation and ABEX2005 (Rhodia) in the semicontinuous experiments. Sodium bicarbonate (PANREAC) was used as buffer in the preparation of the seed. Potassium persulfate (FLUKA Chemika) was used as initiator.

2.2. Emulsion polymerizations

All the semicontinuous reactions were seeded. The poly(BA-co-MMA) seed was prepared batch-wise following the formulation shown in Table 1 in a stainless steel reactor fitted with a sampling device, N₂ inlet and a stainless steel impeller. The reaction was carried out at 65 °C and it was kept overnight at 90 °C with the aim of decomposing the unreacted initiator. Table 1 also shows the properties of the seed polymer.

The semicontinuous emulsion polymerizations were carried out in a 1 L glass jacketed reactor fitted with a reflux condenser, sampling device, N₂ inlet, two feeding inlets and a stainless steel anchor stirrer equipped with two blade impellers rotating at 230 rpm. Table 2 summarizes the formulation used in the semicontinuous experiments. The experimental procedure was as follows: first, the polymer seed and a part of the emulsifier were added into the reactor. When the temperature was 0.5 °C below the reaction temperature set point, half of the initiator was added into the reactor. When the desired reaction temperature was reached, the rest of the

Table 2
Formulation used in the seeded semicontinuous emulsion polymerization of BA/MMA/MAA at 80 °C

Ingredient	Initial charge (g)	Stream 1 (g)	Stream 2 (g)
Seed polymer	32	–	–
Water ^a	161.31	27	245.31
ABEX2005 (surf.)	3.68	–	14.72
Methyl methacrylate	–	–	0–183.24
Butyl acrylate	–	–	183.24–366.48
Methacrylic acid	–	–	3.66
K ₂ S ₂ O ₈	0.276	0.276	–

^a Includes the water contained in the seed.

ingredients were fed. Upon finishing the addition, the reaction was kept batch-wise for 60 min.

2.3. Characterization

Monomer conversion was determined by gravimetry. The instantaneous conversion, X_i , was defined as the amount of polymer (including the polymer in the seed) divided by the amount of monomer and polymer in the reactor. The overall conversion was the amount of polymer (without the polymer in the seed) divided by the total amount of monomer plus polymer in the formulation.

The gel fraction was determined by extraction with THF. The process consisted in a 7 h continuous extraction with THF under reflux in a 2 L glass reactor [6,8]. After the extraction, the samples were dried and the gel content was calculated as the ratio between the dry polymer remaining after the extraction and the initial amount of dry polymer.

The level of branching was measured at 30 ± 1 °C by liquid ¹³C NMR using a Bruker Avance DPX 300 spectrometer with a BBO probe operating at 75.5 MHz. Polymer latexes were dried prior to prepare 100 mg/cm³ solutions in CDCl₃ for analysis. Samples were analyzed with Nuclear Overhauser Effect (NOE) suppression by inverse gate decoupling with a pulse interval of 4 s to allow complete recovery of all carbons and hence the spectra were quantitative [6]. Over 25,000 acquisitions were collected in acquisition times longer than 24 h to have a good signal/noise ratio. Only spectra with a signal/noise ratio of the branching peak (quaternary carbon peak at 47–49 ppm) higher than 10 were considered to compute the level of branches. A ±15% error can be attributed to the measurement [9]. The peaks for all the spectra were referenced to the solvent (CDCl₃) peak at 77 ppm. Fig. 1 shows the 30 < δ < 50 region of a typical spectra of poly(BA-co-MMA) emulsion copolymer. The peak assignment in Table 3 was done according to Pham et al. [10].

The 33 < δ < 42 region containing the resonances for the CH₂ and CH carbons adjacent to the quaternary carbon, C_q, branch point, which are used to calculate the level of branches in the homopolymers of BA [6,11], also contained peaks corresponding to various repeat unit sequences; hence this region could not be used to quantify branching [4]. As an alternative, the level of branching was estimated by referring the quaternary carbon of a branch point to the quaternary carbon of

Table 1
Formulation used to prepare the seed

Ingredient	Amount (g)	Properties
Methyl methacrylate	125	Solids content 20.1%
Butyl acrylate	125	Branching < 0.1%
Water	1000	Gel content < 5%
SLS	5.00	Particle size 67 nm
NaHCO ₃	1.25	
K ₂ S ₂ O ₈	1.25	

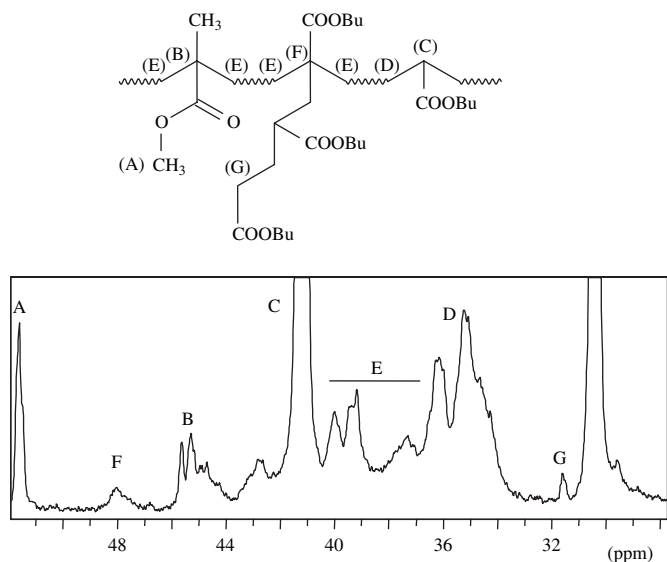


Fig. 1. ^{13}C NMR spectrum of a BA/MMA (90/10 wt/wt) latex produced at 80°C . Peak assignment is given in Table 3.

Table 3
 ^{13}C NMR chemical shift assignments for poly(BA-co-MMA) (50/50 wt%) [10]

Peak	Chemical shift (ppm)	Assignment
A	52.6–54.7	MMA–OCH ₃
B	44.1–47	MMA C _q
C	41.4	BA–BA CH
D	34–36.5	BA–BA CH ₂
E	37.0–40.8	CH ₂ and CH adj. to C _q
F	47–49	Branch C _q
G ^a	31.4	End-group CH ₂ –CH ₂ –COOBu

^a From Ref. [4].

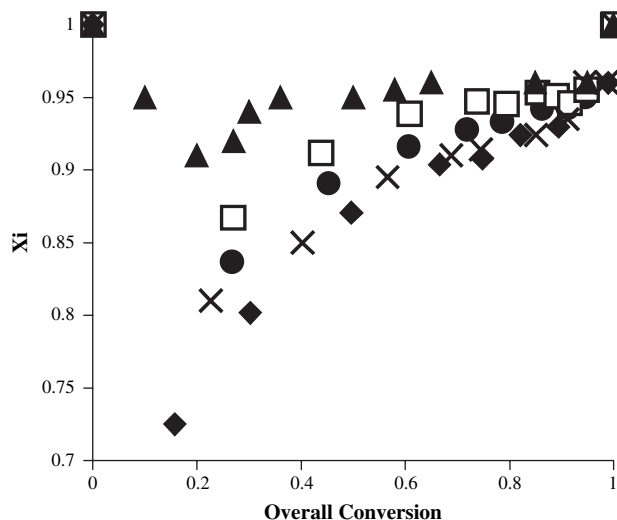


Fig. 2. Effect of monomer ratio in the feed on the evolution of the instantaneous conversion in the seeded semibatch emulsion copolymerization of BA/MMA/MAA carried out with different BA/MMA ratios at 80°C . Legend: \blacklozenge , 50/50; \times , 75/25; \bullet , 90/10; \square , 95/5; and \blacktriangle , 100/0.

the MMA unit (see Table 3 for the peak assignment) assuming that the final composition of the copolymer chains corresponds to the BA/MMA monomer ratio in the formulation, which is a fairly good assumption because the conversion was almost 100% in all polymerizations as shown in Fig. 2.

The following expression was used for computing the level of branching:

$$\%C_q = \frac{A_{C_q\text{BA}}}{A_{C_q\text{MMA}}} X_{\text{MMA}} \times 100 \quad (1)$$

where A_i is the area of each peak of the spectrum and X_{MMA} is the molar fraction of MMA in the formulation.

On the other hand, in the case of the pure BA homopolymer, the level of branching was calculated following the method described in the literature [6,11].

3. Results and discussion

Before discussing the results it is worth describing the mechanisms that lead to the formation of branches (short and long) and gel polymer in the emulsion polymerization of BA and MMA. Scheme 1 displays these mechanisms.

Branches in the homopolymerization of BA are formed by backbiting (short chain branches, SCB, reaction 1b) and intermolecular chain transfer to polymer (long chain branches, LCB, reaction 2), but the former is the predominant mechanism [5–7]. The backbiting reaction competes with propagation (see reactions 1a and 1b) and hence the lower the monomer concentration in the polymer particles the higher the branches formed by backbiting. Intermolecular chain transfer to polymer (reaction 2) requires labile H in the backbone of the polymer chains. In poly(BA-co-MMA) copolymers the abstractable H comes from the BA units in the backbone and hence as MMA is increased in the formulation, the number of sites for abstraction is reduced.

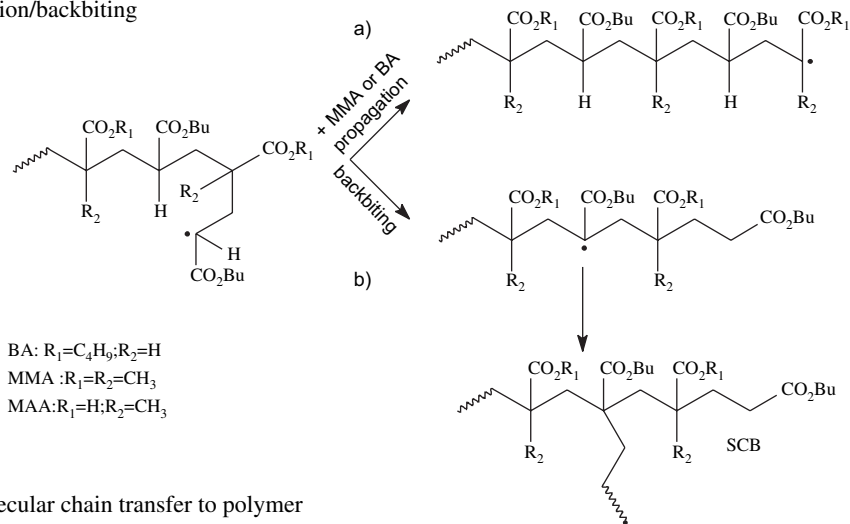
The branched radicals can terminate either by disproportionation or by combination (reaction 3). If a chain-end radical terminates in a BA unit, combination is more likely, but if the chain-end radical terminates in an MMA unit, disproportionation will preferentially occur [12]. Gel polymer can only be formed if the termination occurs in some non-negligible extent by the combination mechanism.

3.1. Polymerization kinetics

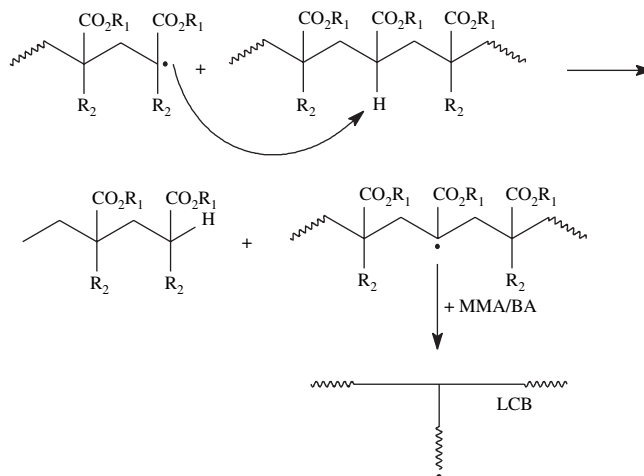
Fig. 2 shows the evolution of the instantaneous conversion in the experiments carried out with different BA/MMA ratios at 80°C .

It can be seen that polymerization rate decreased as the concentration of MMA increased because of the lower propagation rate coefficient of MMA as compared with that of BA [13–15]. However, the opposite trend was found by Elizalde et al. [3]; namely, increasing MMA led to an increase of the instantaneous conversion. The different trends can be explained by the lower initiator concentration (0.13 wt% in this work versus 0.30 wt%) and the smaller particle size of

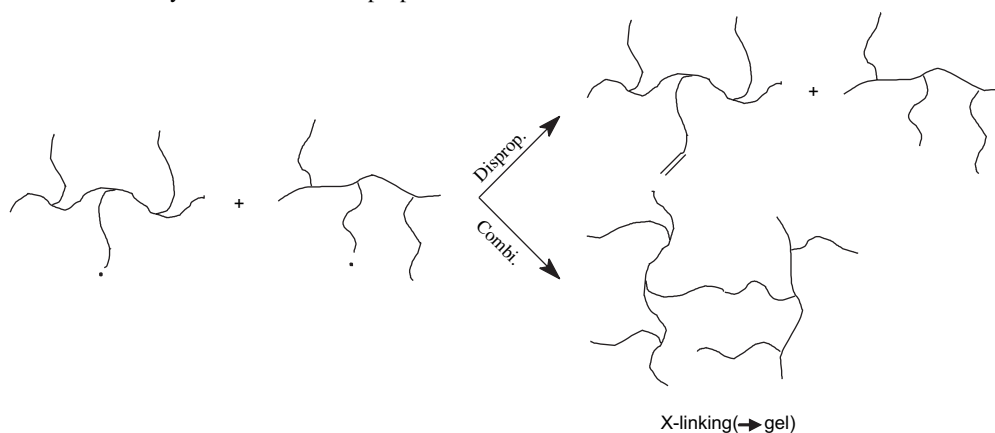
1. Propagation/backbiting



2. Intermolecular chain transfer to polymer



3. Termination by combination or disproportionation



Scheme 1.

the seed polymer (67 nm in this work versus 82–89 nm) employed in this work, which made the average number of radicals per particle insensitive to the MMA feed composition. Thus, the decrease of the average propagation rate constant by increasing the MMA content of the feed [13–15] explains the decrease in the polymerization rate.

3.2. Gel content

Fig. 3 displays the final gel content of the BA/MMA copolymer latexes produced with different BA/MMA ratios. It can be seen that as the amount of MMA increased the gel content decreased. As shown in Scheme 1 gel is formed by

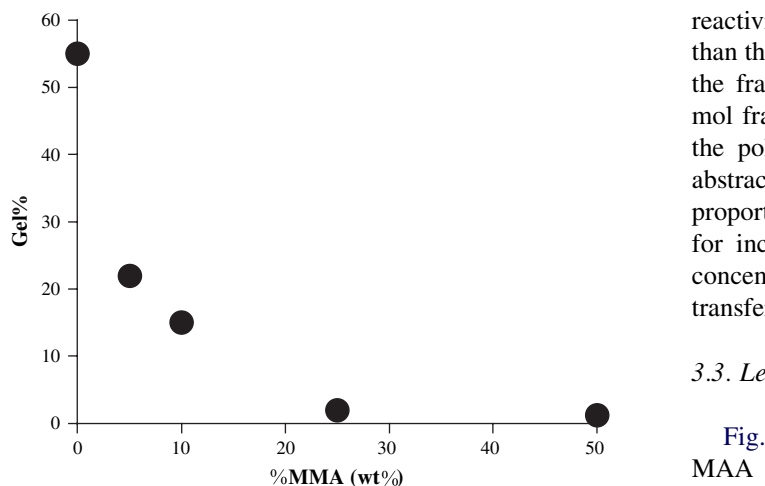


Fig. 3. Final gel content of BA/MMA/MAA copolymer latexes produced with different BA/MMA ratios at 80 °C.

intermolecular chain transfer to polymer followed by termination by combination [5,6]. The presence of MMA affected this two-step mechanism in several ways. (i) The MMA radicals are tertiary radicals and hence are much less reactive for hydrogen abstraction than the secondary BA radicals; (ii) the

reactivity ratio of the MMA terminated radicals was higher than that of BA [13] ($r_{\text{MMA}} = 2.24$ and $r_{\text{BA}} = 0.414$), therefore the fraction of MMA terminated radicals is higher than the mol fraction of MMA in the formulation; (iii) MMA units in the polymer backbone do not have labile hydrogens to be abstracted; (iv) MMA radicals preferentially terminate by disproportionation; and (v) instantaneous conversion decreased for increasing MMA contents, leading to a lower polymer concentration, which resulted in a lower intermolecular chain transfer to polymer rate (this was a minor effect).

3.3. Level of branches

Fig. 4 shows the ^{13}C NMR spectra of different BA/MMA/MAA copolymer latexes. It can be observed that the peak corresponding to the quaternary carbon from the branch point ($\delta = 47\text{--}49$ ppm) reduced its intensity as the amount of MMA increased. Using the data shown in these plots the level of branches was estimated and the results obtained are summarized in Table 4.

It is worth pointing out that, in the case of the 50/50 MMA/BA polymer, the peak corresponding to the quaternary carbon of the branch point was not unique ($\delta = 47\text{--}49$ ppm) and therefore, the level of branches was not determined.

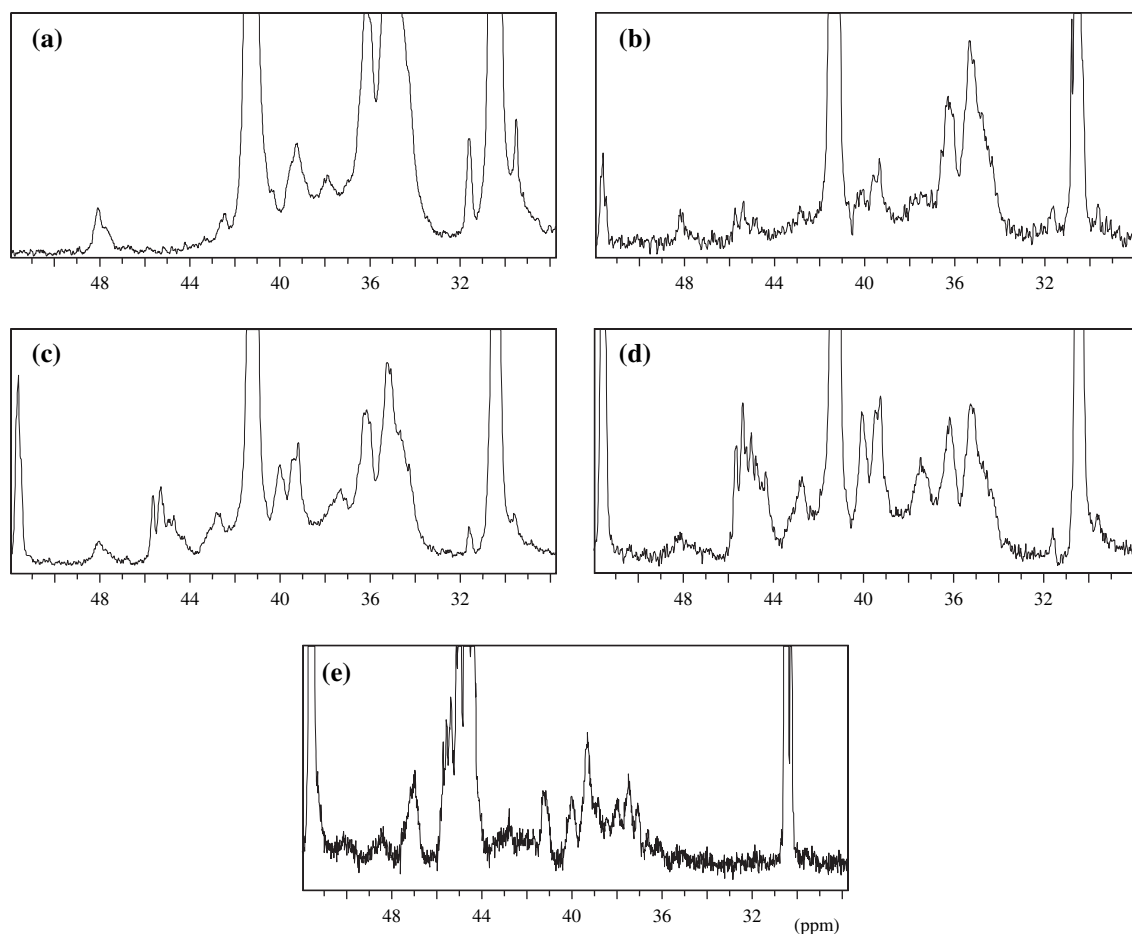


Fig. 4. ^{13}C NMR spectra of BA/MMA/MAA copolymer latexes produced at 80 °C with different amounts of MMA. Legend: (a) 0 wt%; (b) 5 wt%; (c) 10 wt%; (d) 25 wt%; and (e) 50 wt%.

Table 4
Level of branches calculated for BA/MMA latexes produced at 80 °C with different amounts of MMA

BA/MMA wt/wt	Level of branches (%)
100/0	2.6 ± 0.4 ^a
95/5	2.1 ± 0.3 ^a
90/10	1.8 ± 0.2 ^a
75/25	0.3 ± 0.05 ^a
50/50	—

^a Calculated assuming a ±15% error in the measurement [9].

It can be seen that the level of branching decreased from 2.6% for pure BA (in agreement with data from other works [5,6,16,17]) to zero for a 50 wt% of MMA. An additional qualitative proof of this effect comes from the peak at $\delta = 31.4$ ppm corresponding to the CH₂CH₂COOBu end-group [4]. The carbons of the CH₂ groups of the CH₂CH₂COOBu end-groups formed by backbiting appear at $\delta = 31.4$ ppm in the ¹³C NMR spectrum (see Table 3). Fig. 4 clearly displays the decrease in the intensity of this peak as the copolymer composition increased in MMA and for the spectrum of the 50/50 BA/MMA copolymer (Fig. 4e) the peak is not present at all.

To understand the effect of MMA on reducing the level of branching, it is worth recalling that the branches in the homopolymerization of BA are predominantly formed by intramolecular transfer to polymer (backbiting, see reaction 1 in Scheme 1), the contribution of intermolecular chain transfer to polymer being significantly lower [5–7,17,18]. Backbiting occurs predominantly through a six-member centered ring transition state; namely, the last three monomer units of the chain participate in this mechanism. When MMA is copolymerized with BA, the number of BA–BA–BA triads is reduced. The BA–MMA–BA triad may, in principle, backbite, although the rate of backbiting would likely be lower due to the steric effect of the methyl group of the MMA unit that makes difficult the formation of the six-member ring transition state. Furthermore, the addition of MMA to the formulation reduced the instantaneous conversion, increasing the monomer concentration in the polymer particles, which in turn reduced the probability of backbiting [6,16,17].

4. Conclusions

The effect of the monomer feed composition on the kinetics and the microstructural properties of BA/MMA emulsion copolymers was studied. It was observed that the addition of increasing amounts of MMA led to the decrease of the instantaneous conversion because of the lower propagation rate coefficient of the MMA as compared to that of BA.

The higher the amount of MMA the lower the gel content. The presence of MMA affected in several ways gel formation, but likely the main reasons are the lower reactivity of the MMA terminated chains for hydrogen abstraction, the absence of abstractable hydrogens in the MMA units and the fact that MMA radicals terminate by disproportionation. The level of branches also decreased in the presence of increasing amounts of MMA mainly because of the lower reactivity of MMA in terms of intramolecular transfer to polymer. However, the decrease of the probability of having BA–BA–BA triads necessary for the backbiting (the major branching mechanism) and the increase of the monomer concentration in the polymer particles also contributed to decrease backbiting.

Acknowledgements

The authors thank the financial support provided by the Industrial Liaison Program in polymerization in dispersed media of POLYMAT (Arkema, Cytec Surface Specialties, Dow, Euroresin, Nuplex Resins, Rohm and Haas and Wacker Chemie).

References

- [1] Sayer C, Lima EL, Pinto JC, Arzamendi G, Asua JM. *J Polym Sci Part A Polym Chem* 2000;38:1100–9.
- [2] Parouti S, Kammona O, Kiparissides C, Bousquet. *J Polym React Eng* 2003;11:829–53.
- [3] Elizalde O, Leiza JR, Asua JM. *Ind Eng Chem Res* 2004;43:7401–9.
- [4] Britton DJ, Lovell PA, Heatley F, Venkatesh R. *Macromol Symp* 2001; 175:95–104.
- [5] Plessis C, Arzamendi G, Leiza JR, Schoonbrood HAS, Charmot D, Asua JM. *Macromolecules* 2000;33:4–7.
- [6] Plessis C, Arzamendi G, Leiza JR, Schoonbrood HAS, Charmot D, Asua JM. *Macromolecules* 2000;33:5041–7.
- [7] Farcet C, Belleney J, Charleux B, Pirri R. *Macromolecules* 2002;35: 4912–8.
- [8] Plessis C, Arzamendi G, Leiza JR, Alberdi JM, Schoonbrood HAS, Charmot D, et al. *J Polym Sci Part A Polym Chem* 2001;39:1106–19.
- [9] Plessis C, Arzamendi G, Alberdi JM, Agnely M, Leiza JR, Asua JM. *Macromolecules* 2001;34:6138–43.
- [10] Pham QT, Pétiaud R, Waton H, Llauro-Darricades MF. *Proton and carbon NMR spectra of polymers*, vol. 3. Chichester, UK: John Wiley & Sons; 1984.
- [11] Ahmad NM, Heatley F, Lovell PA. *Macromolecules* 1998;31:2822–7.
- [12] Li DH, Grady MC, Hutchinson RA. *Ind Eng Chem Res* 2005;44: 2506–17.
- [13] Hutchinson RA, McMinn JH, Paquet DA, Beuermann S, Jackson C. *Ind Eng Chem Res* 1997;36:1103–13.
- [14] Beuermann S, Buback M, Davis TP, Gilbert RG, Hutchinson RA, Olaj OF, et al. *Macromol Chem Phys* 1997;198:1545–60.
- [15] Asua JM, Beuermann S, Buback M, Castignolles P, Charleux B, Gilbert RG, et al. *Macromol Chem Phys* 2004;205:2151–60.
- [16] Gonzalez I, Leiza JR, Asua JM. *Macromolecules* 2006;39:5015–20.
- [17] Plessis C, Arzamendi G, Alberdi JM, van Herk AM, Leiza JR, Asua JM. *Macromol Rapid Commun* 2003;24:173–7.
- [18] Peck ANF, Hutchinson RA. *Macromolecules* 2004;37:5944–51.