

Bifunctional Initiators on the Polymerization of Vinyl Acetate

Eduardo Galharo, Cilene Meinberg Franco, Liliane M. F. Lona

Department of Chemical Processes, School of Chemical Engineering, University of Campinas, Campinas, São Paulo 13083852, Brazil

Correspondence to: E. Galharo (E-mail: eduardo@feq.unicamp.br)

ABSTRACT: Initiators with functionality bigger than one can be used in free radical polymerization (FRP) to increase the polymerization rate without decreasing the molecular weight of the polymer. The use of bifunctional initiators to produce linear polymers (like polystyrene and Poly(methyl methacrylate) (PMMA)) can be found in the literature; however, their application to produce branched polymers is rarer. This work reports the effect of the bifunctional initiator Luperox 531 (1.4-bi(t-butyl-carboperoxide) cyclehexane) on the FRP of vinyl acetate, which produces branched polymers. The monofunctional initiator Luperox TBEC (tert-butylperoxide-2-ethylhexil carbonate) is also used as base of comparison. Polymerizations in ampoules have been performed in different temperatures and initiator concentrations. Results were compared to those obtained from the styrene polymerization, which produces linear chains. It can be concluded that the effect of bifunctional initiators on FRP depends strongly on the kinetic mechanism, kind of monomer, and operating conditions adopted. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: bifunctional initiators; free radical polymerization; vinyl acetate

Received 31 May 2011; accepted 13 April 2012; published online

DOI: 10.1002/app.37907

INTRODUCTION

To increase the free radical polymerization (FRP) rate, an increase either in the temperature or in the initial concentration of the initiator can be used; however, both alternatives generate more radicals on the system and, as a consequence, polymers with lower molecular weights are obtained. As well known, an alternative to simultaneously increase polymerization rate and molecular weights is to use bifunctional initiators.

There are many papers in literature dealing with bifunctional initiator in both experimental and simulation levels; however, most of them consider monomers that generate linear polymers, usually styrene and methyl methacrylate.^{1–6} A few works in literature deal with bifunctional initiator and monomers different from styrene and MMA. For example, Krallis et al.⁷ polymerize vinyl chloride, Naghash and Mallakpour⁸ copolymerize methyl methacrylate and ethylene glycol dimethacrylate, and Dhib et al.⁹ and Cavin et al.¹⁰ work with ethylene that also produces branches when polymerized. Scora et al.¹¹ copolymerize butylacrylate and vinyl acetate, but they use a tetrafunctional initiator. Machado and Lona¹² deal with homopolymerization of styrene and vinyl acetate using bifunctional initiator; however, their research is only in simulation level. Notwithstanding, as long as we know, there is no experimental work in literature

dealing with homopolymerization of vinyl acetate and a bifunctional initiator.

It has been observed that the performance of bifunctional initiators depends on the monomer used and on the operating conditions considered. For example, since styrene polymerization presents termination by combination only, the increase in polymer molecular weight when changing from mono- to bifunctional initiator is much more effective when compared to the polymerization of methyl methacrylate, which also presents termination by disproportionation. Termination by combination generates longer chains so the bifunctional initiators can intensify this effect.

Vinyl acetate is a monomer that presents termination by combination and disproportionation and transfer to monomer and polymer, which generate branches. In this study, this monomer was considered due to the complexity of its kinetic mechanism. The obtained results are compared with those obtained from the polymerization of styrene.

The study, in experimental level, of bifunctional initiators in the polymerization of vinyl acetate is new in literature. This case study seems to be very comprehensive, because the kinetic mechanism brings many steps different from what occurs with

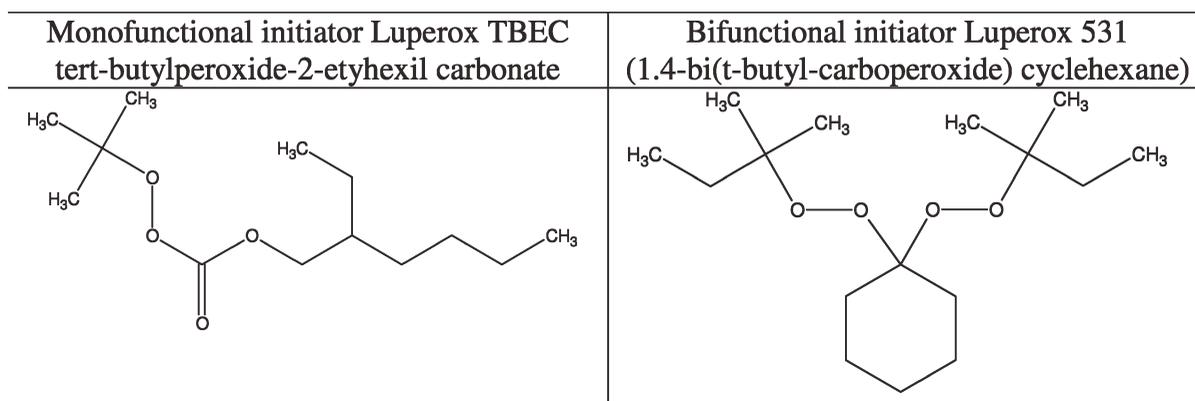


Figure 1. Chemical structure of mono and bifunctional initiators.

styrene, MMA, and many other monomers considered in literature for the study of bifunctional initiators.

EXPERIMENTAL DESIGN

The chemical structure of mono and bifunctional initiators used in this work is shown in Figure 1.

The polymerization is performed in glass ampoules in different temperatures and initiator concentrations using purified monomer. To do that, the monomer was washed three times with a 10% NaOH solution and deionized water. After washing, the monomer was placed in a flask with calcium chloride that acts as drying agent. The next step was the monomer distillation under vacuum. Desired quantities of monomer (styrene or vinyl acetate) and initiator [Luperox TBEC (tert-butylperoxide-2-ethylhexyl carbonate) or Luperox 531] were weighed, added in beakers, and transfer to ampoules.

The ampoules were degassed by three cycles of freezing and thawing under vacuum. Each ampoule was sealed using a torch with fire. The ampoules were placed in a bath of heat oil at a certain temperature, where polymerization occurs. The ampoules were withdrawn at various pre-established intervals of time, and placed in an ice bath and then in liquid nitrogen to stop the reaction. After weighing, the mixture was removed from the ampoules using methylene chloride.

The mixture polymer/monomer was dissolved in methylene chloride and precipitated with ethanol. After evaporation of solvent and

residual monomer, under vacuum dryer, the conversion is obtained by gravimetry. The samples were transferred to vials for analysis in a gel permeation chromatograph with a triple detector: refraction index, viscosimeter, and right-angle laser light scattering.

RESULTS AND DISCUSSIONS

Tables I and II bring the experimental conditions used for the polymerization of styrene and vinyl acetate. Two different levels of initiator concentration and temperature were considered for both cases.

The lower and higher temperatures were 115 and 125°C for both monomers. For the initial concentration of the initiator, the lower and higher levels were 0.00145 and 0.0029 mol/L for the styrene case and 0.0005 and 0.00025 mol/L for the vinyl acetate case. It can be seen that Table II presents fewer operating conditions, because many ampoules exploded during the polymerization. However, the experiments performed in this study were enough to conclude and understand the results. It is difficult to work with vinyl acetate and frequent explosion of glass ampoule when working with vinyl acetate was also observed by other researches. However, this is not a common behavior when dealing with styrene polymerization.

The constant for the dissociation (k_d) of both initiators follows the Arrhenius law, and the values of activation energy (E) and pre-exponential factor (A) can be seen in Table III.

For the bifunctional initiator L531, both constants for the peroxide group dissociation are the same ($k_{d1} = k_{d2}$).

The effect of bifunctional initiator on the polymerization of vinyl acetate monomer is not inferred directly. On one hand,

Table I. Experimental Conditions for the Polymerization of Styrene

Run	Initiator	T (°C)	Concentration of initiator (mol/L)
1	TBEC	115	0.0029
2	TBEC	125	0.0029
3	L531	115	0.0029
4	L531	125	0.0029
5	L531	115	0.00145
6	L531	125	0.00145
7	TBEC	115	0.00145
8	TBEC	125	0.00145

Table II. Experimental Conditions for the Polymerization of Vinyl Acetate

Run	Initiator	T (°C)	Concentration of initiator (mol/L)
9	TBEC	115	0.0005
10	L531	115	0.0005
11	TBEC	125	0.0005
12	L531	125	0.0005
13	L531	115	0.00025

Table III. Kinetic Parameters of Both Initiators

Initiator	A (l/min)	E (cal/mol)	k_d (at 115°C)	k_d (at 125°C)
L531	4.847×10^{17}	34,580.0	1.072×10^{13}	1.403×10^{13}
TBEC	3.389×10^{15}	31,494.0	1.950×10^{11}	2.493×10^{11}

the reaction of transfer to monomer and termination by disproportionation reduces the impact of the bifunctional initiator on producing long chains, similar to what happens with the methyl methacrylate polymerization (see discussion in the Introduction section). On the other hand, the transfer to polymer and monomer reaction, which is able to produce branches in chains, can increase the effect of bifunctional initiators on generating longer chains. Transfer to polymer does not change the number of radicals present in the system, but it increases the molecular weight and its distribution.

Figures 2 and 3(a,b) show conversion of styrene and vinyl acetate versus time for both kinds of initiators. For the styrene polymerization, the temperature is equal to 125°C and initiator concentration is equal to 0.0029 mol/L. For the vinyl acetate case, the initiator concentration is 0.0005 mol/L and two different temperatures were considered ($T = 115$ and 125°C). As expected, it can be observed that it is possible to obtain faster polymerization rates when a bifunctional initiator is used for the two kinds of monomer.

Figures 4–6 show the average molecular weights and the polydispersity of polystyrene and Polyvinyl acetate (PVA). It can be noticed that a polymer with higher molecular weight can be obtained when a bifunctional initiator is used for the styrene polymerization; however, the molecular weights almost do not change with the kind of initiator, for the two temperatures considered, when dealing with the vinyl acetate polymerization.

It is known that a monofunctional initiator presents only one bond O—O and a bifunctional initiator presents two. On one hand, chains obtained with bifunctional initiators should be shorter than those obtained with the monofunctional initiator

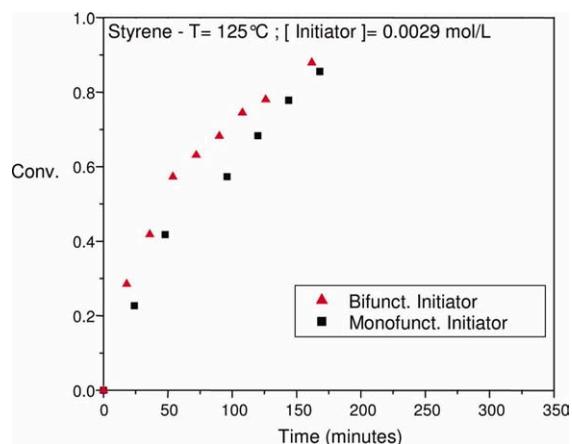


Figure 2. Conversion of styrene versus time. Temperature equal to 125°C and concentration of initiator equal to 0.0029 mol/L. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

due to a larger generation of radicals, besides, the L531 initiator presents higher k_d . However, the species that contain diradicals will grow up from both sides of the chain, reaching longer length. The combination of these two effects generates a polymer with higher molecular weights when bifunctional initiators are used in the styrene polymerization, as shown in Figure 4(a).

The molecular weights of PVA for the polymerization at 115 and 125°C can be seen in Figures 5(a) and 6(a). It can be observed, for both temperatures, that the molecular weights were less affected by the kind of initiator being used, different from what happened with the styrene polymerization. Although the transfer to polymer reaction generates some bigger chains [see in Figure 5(a) how the \bar{M}_w increases rapidly with time], the transfer to monomer and termination by disproportionate steps may reduce the size of other chains when compared with styrene polymerization, for example [see the high polydispersity in Figures 5(b) and 6(b)], making the bifunctional initiator not so efficient in increasing molecular weight as occurred with styrene polymerization. One interesting fact to be observed is that, in the case of vinyl acetate, we worked with lower concentration of initiator (0.0005 mol/L for the vinyl acetate case and 0.0029 or 0.00145 mol/L for the styrene case). As previously seen,⁶ the lower concentration of initiator makes the breaking of the second peroxide more effective, generating higher molecular weights. Even in this condition, important differences on the behavior of mono and bifunctional initiators could not be seen.

It can be observed that the temperature has less effect on conversion (see Figure 3) than on molecular weights [see Figures 5(a) and 6(a)] for both initiators and that the molecular weights increase drastically when temperature is 115°C. It is well known that the lower the temperature, the lower the initiator dissociation, which generates a lower amount of chains (higher molecular weights). This can be confirmed in the first stages of Figures 5(a) and 6(a) (the \bar{M}_w for $T = 125^\circ\text{C}$ is almost half of the one for $T = 115^\circ\text{C}$). At certain conversion, the transfer to polymer reaction becomes more frequent, some chains become bigger and the gel effect becomes more important. All these effects are more important for lower temperatures, explaining the different behavior between Figures 5(a) and 6(a).

Figure 7(a and b) show conversions of vinyl acetate and styrene respectively versus time for both initiators, but considering lower temperature when a bifunctional initiator is used. It can be observed that there is an economical advantage when working with bifunctional initiators, because the reactor can operate at temperatures at least 10°C lower, which represents cost reduction.

Figure 8 shows the average molecular weight profiles for polyvinyl acetate and polystyrene when working with lower temperature for the bifunctional initiator.

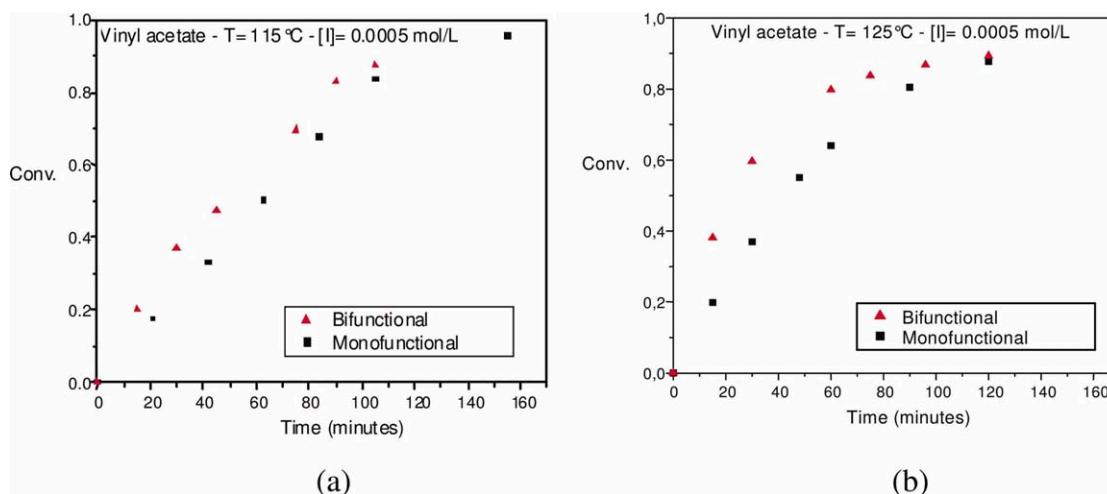


Figure 3. Effect of initiator on conversion of vinyl acetate considering $[I] = 0.0005 \text{ mol/L}$. (a) Temperature equal to 115°C and (b) Temperature equal to 125°C . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

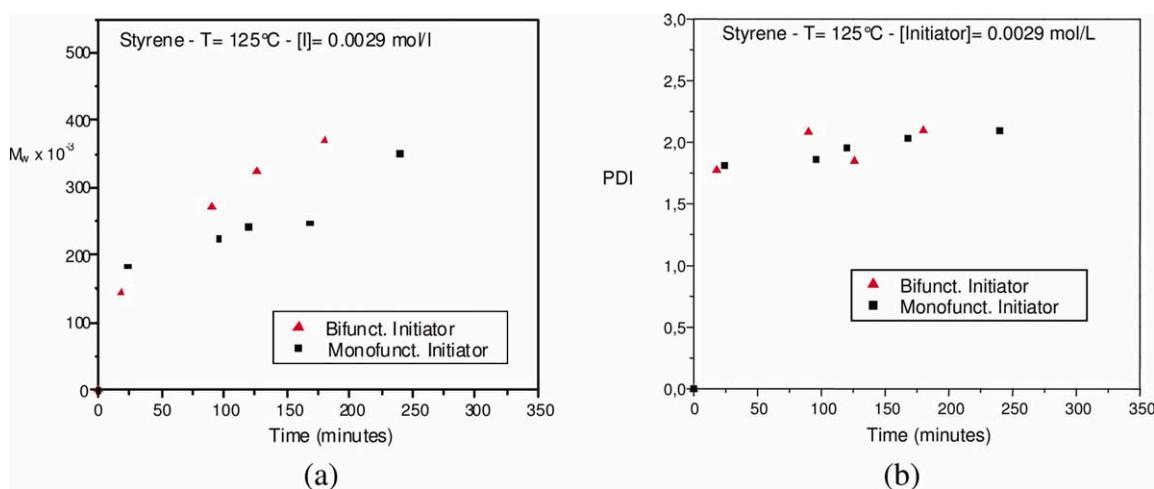


Figure 4. Styrene polymerization using mono and bifunctional initiator at $[I] = 0.0029 \text{ mol/L}$ and $T = 125^\circ\text{C}$. (a) Average molecular weight and (b) Polydispersity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

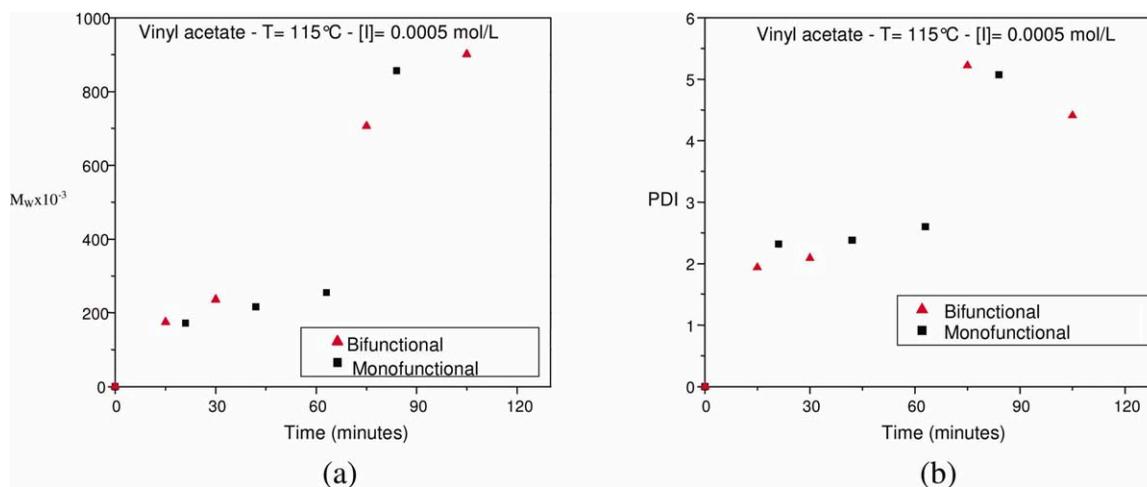


Figure 5. Vinyl acetate polymerization using mono and bifunctional initiator at $[I] = 0.0005 \text{ mol/L}$ and $T = 115^\circ\text{C}$. (a) Average molecular weight and (b) Polydispersity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

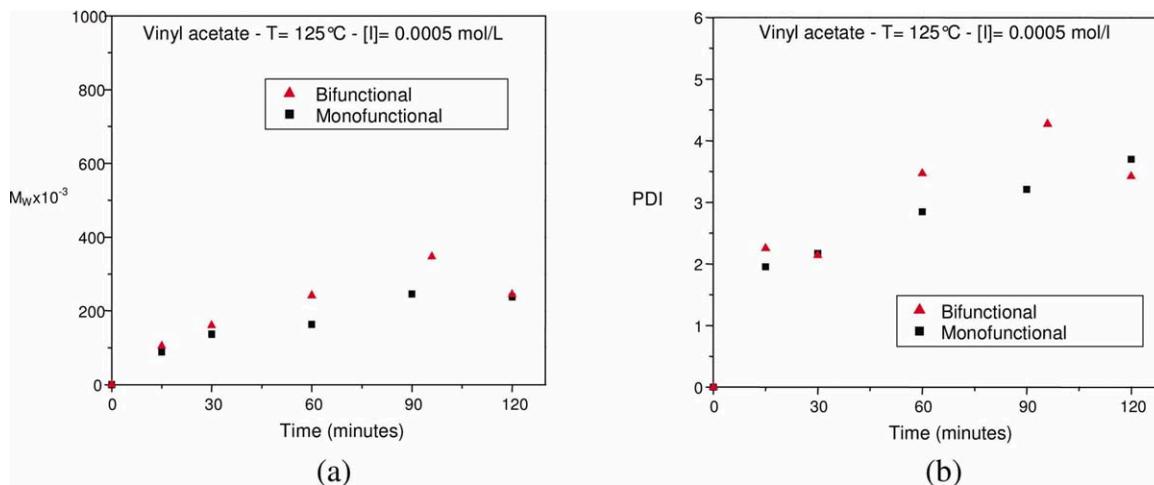


Figure 6. Vinyl acetate polymerization using mono and bifunctional initiator at $[I] = 0.0005 \text{ mol/L}$ and $T = 125^\circ\text{C}$. (a) Average molecular weight and (b) Polydispersity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

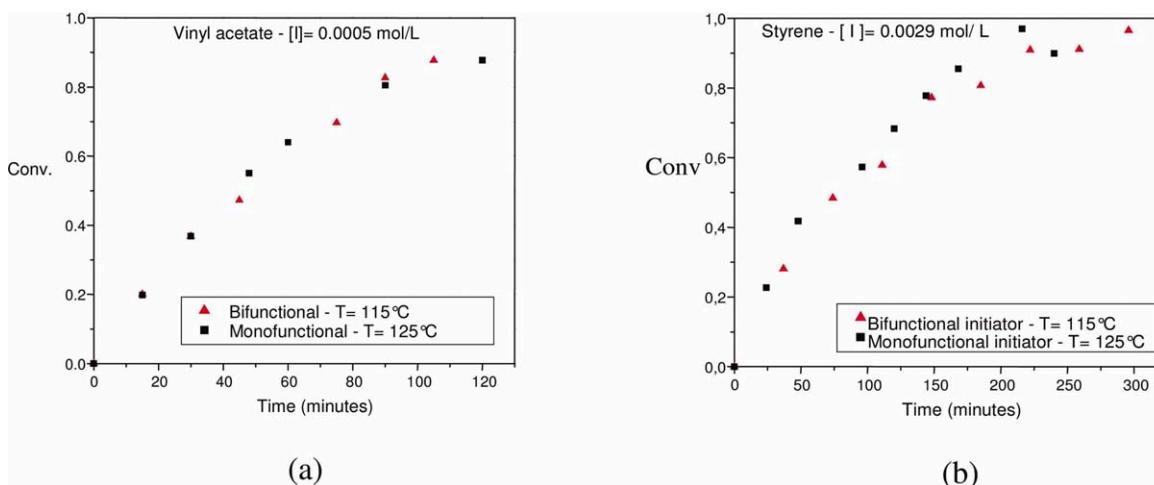


Figure 7. (a) Conversion of vinyl acetate versus time at different temperatures and $[I] = 0.0005 \text{ mol/L}$; (b) Conversion of styrene versus time at different temperatures and $[I] = 0.0029 \text{ mol/L}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

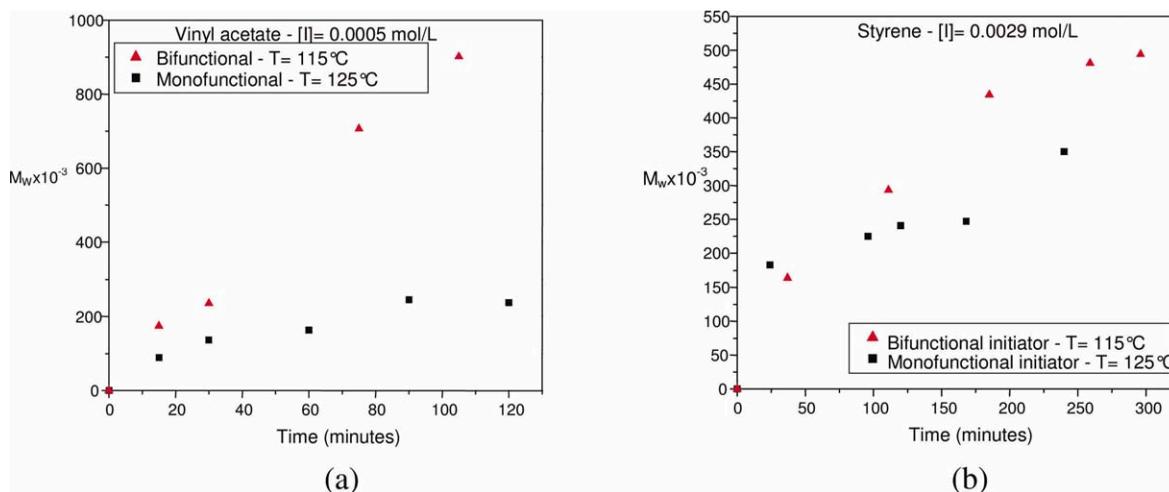


Figure 8. (a) \bar{M}_w versus time for the vinyl acetate polymerization at different temperatures and $[I] = 0.0005 \text{ mol/L}$; (b) \bar{M}_w versus time for styrene polymerization at different temperatures and $[I] = 0.0029 \text{ mol/L}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

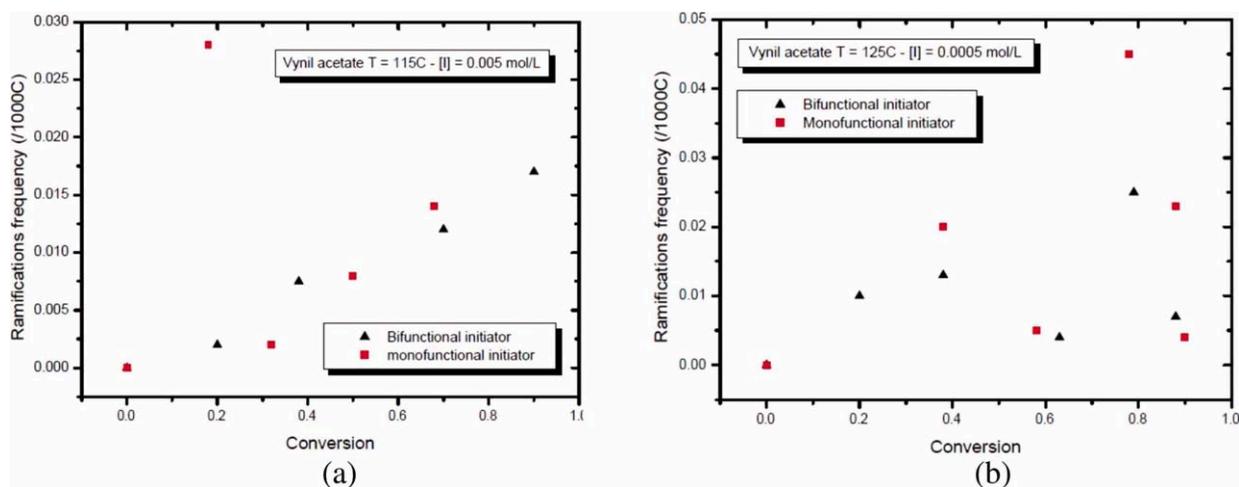


Figure 9. Ramifications frequency versus conversion for each set of 1000C. Temperatures equal to 115 and 125°C for (a) and (b), respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In spite of having similar conversion profiles, it is possible to obtain polymers with higher molecular weights, when working with bifunctional initiator at lower temperature. This effect is more evident for the case of PVA, where we can see a more pronounced increase in M_w when bifunctional initiator is used at lower temperature.

When working with L531 at lower temperatures, fewer radicals are generated, but diradicals are still formed. These effects corroborate to the more pronounced increase in molecular weights.

The polydispersity is almost the same when polymerization using bifunctional initiator is performed at a lower temperature (not shown).

Figure 9 shows the ramifications frequency in relation to the number of carbons (C) present in the molecule.

Analyzing the Figure 9, it can be seen that when the bifunctional initiator is used, there are no alterations in relation to number of ramifications in comparison to the monofunctional initiator. This point can be explained easily by the fact of the chemical structure of the bifunctional initiator be not favorable for the ramifications production, perhaps differently of what would be observed by dealing with a tetrafunctional initiator. Still by means of the Figure 9, it can be noticed that there is some oscillation for the points of higher values, what possibly was provoked by the heterogeneity of the samples.

CONCLUSIONS

In this study, the effect of bifunctional initiators was analyzed for the vinyl acetate polymerization, which produces polymer with branches. Results were compared to those obtained from the styrene polymerization, which produces linear chains.

It can be concluded that the effect of bifunctional initiators on FRP depends strongly on the kinetic mechanism and kind of

monomer. The operating conditions adopted also have influence on the performance of bifunctional initiators.

ACKNOWLEDGMENTS

The authors acknowledge the financial support provided by FAPESP (State of Sao Paulo Research Foundation—Brazil).

REFERENCES

- Villalobos, M. A.; Hamielec, A. E.; Wood, P. J. *Appl. Polym.* **1991**, *42*, 629.
- Yoom, W. J.; Choi, K. Y. *J. Appl. Polym.* **1992**, *46*, 1353.
- Dhib, R.; Gao, J.; Penlidis, A. *Polym. React. Eng.* **2000**, *8*, 299.
- Wu, J.; Sheng, W.; Shan, G.; Huang, Z.; Weng, Z. *Huagong Xuebao/J. Chem. Industry Eng. (China)* **2005**, *56*, 358.
- Sheng, W.; Weng, Z.; Qi, D.; Zhou, Z. *Acta Chimica Sinica* **2009**, *67*, 335.
- Machado, P. F. M. P. B.; Lona, L. M. F. *J. Appl. Polym. Sci.* **2010**, *117*, 2803.
- Krallis, A.; Kotoulas, C.; Papadopoulos, S.; Kiparissides, C.; Bousquet, J.; Bonardi, C. *Ind. Eng. Chem. Res.* **2004**, *43*, 6382.
- Naghash, H. J.; Mallakpour, S. *Iranian Polym. J.* **2004**, *13*, 287.
- Dhib, R.; Al-Nidawy, N. *Chem. Eng. Sci.* **2002**, *57*, 2735.
- Cavin, L.; Rouge, A.; Meyer, T.; Renken, A. *Polymer* **2000**, *41*, 3925.
- Scorah, M. J.; Cosentino, R.; Dhib, R.; Penlidis, A. *Polym. Bull.* **2006**, *57*, 157.
- Machado, P. F. M. P. B.; Lona, L. M. F. *Comput. Aided Chem. Eng.* **2010**, *20*, 445.