

## Solution styrene polymerizations performed with multifunctional initiators

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**ABSTRACT:** This paper analyzes the performance of multifunctional initiators frequently used in the literature and in the industry for the production of polystyrene (PS). Polymerizations of styrene in ethylbenzene were conducted in batch at high temperatures (120°C) until conversions around 70%, as frequent in industrial sites. Polymerizations were conducted in glass test ampoules with different concentrations and types of initiators, parameterized in terms of the active oxygen concentration. The results showed that when used at similar active oxygen concentrations, the use of the tetrafunctional initiator tetrakis(tertbutylperoxy carbonate) can allow for the production of polymer resins with significant higher average molar masses with similar polymerization rates, which can be very useful at plant site for the modification of polymer grades. Besides, the results show that the decomposition of one peroxide group of the analyzed multifunctional initiators does not affect the rates of decomposition of the remaining ones significantly, as reaction proceeds as initiated by a monofunctional initiator. Finally, although described in previous styrene polymerization studies, the use of the trifunctional initiator 3,6,9-triethyl 3,6,9-trimethyl-1,4,7 triperoxonane is difficult to justify in commercial units, given its very high half-life time. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42609.

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### INTRODUCTION

The use of multifunctional initiators in free radical polymerization processes can allow for the production of polymer materials with higher average molar masses at higher reaction rates (when compared with similar monofunctional initiators), giving flexibility for modification and design of the mechanical and structural properties of the polymer grades produced at plant site.<sup>1–7</sup> However, application of multifunctional initiators is predominantly performed in styrene polymerizations, mainly in bulk and solution processes.<sup>1,8–15</sup>

Multifunctional initiators can be defined generically as chemical compounds that contain more than one unstable chemical function (normally azo or peroxide) and therefore can generate more than two free radicals when they decompose (usually thermally). The number of radicals generated and the rate of decomposition can depend on the reaction stage, operation conditions, and chemical properties of the unstable groups.<sup>16</sup> The proper selection of the employed multifunctional initiators can allow for improved control of the molecular properties of the final resin, including the average molar masses and the chain size distributions.<sup>17,18</sup>

In the 1970's, the Pennwalt Corporation Company filed several patents for the production of bifunctional initiators.<sup>19–23</sup> The main idea behind these patents was the modification of polymer properties and the improvement of quality control procedures at plant site through utilization of multifunctional peroxides, as analyzed originally by Yenal'ev *et al.*<sup>1</sup> and studied intensively throughout the 1970's and beginning of 1980's.<sup>24–26</sup> Particularly, Kuchanov *et al.*<sup>17</sup> evaluated the performances of monofunctional, bifunctional, and trifunctional initiators with similar chemical structures in styrene bulk polymerizations, finding that similar reaction rates could be obtained when similar concentrations of peroxide groups were used.

Since the late 1980's, several studies have been published regarding the use of multifunctional initiators in different polymerization processes, including characterization and applications of the obtained polymer materials and the mathematical modeling of the reaction system, although the vast majority of these studies has been focused on the PS production.<sup>8–15</sup> Since the beginning of the 21<sup>st</sup> century, experimental and modeling studies related to the use of multifunctional initiators (bi, tri, and tetrafunctional molecules) in polymerization processes have been extended to other styrene,<sup>8,12–14,27–29</sup> methyl methacrylate (MMA),<sup>5,6,30</sup> vinyl

chloride,<sup>31,32</sup> vinyl acetate,<sup>7,33</sup> and styrene/MMA copolymerization systems.<sup>6,34</sup> Despite that, it seems correct to say that the commercial use of multifunctional initiators in free radicals polymerization reactions is related primarily to styrene bulk polymerization reactions.

Yoon<sup>35</sup> studied the production of PS through solution polymerization of styrene in ethylbenzene using a mixture of symmetrical bifunctional initiators. Reactions were performed continuously in a reaction train comprising a stirred tank reactor (CSTR) and a tubular reactor. A mathematical model was developed and implemented successfully to represent the available experimental data. Chien<sup>2</sup> and Almeida *et al.*<sup>36</sup> extended Yoon's model afterward to investigate the sensitivity of model performance at the steady-state condition to the modification of process parameters.

In spite of all the activity in this field, no published studies investigate the performances of different multifunctional initiators in the polymerization of styrene in a comparative manner. Modeling and experimental studies normally analyze the effects of a single type of multifunctional initiator (or mixture of initiators) on the process performance, without making reference to the performances of other initiation systems in similar conditions. For this reason, it is usually very difficult to compare the performances of different initiation systems on a fair common basis, using only the available published information.

Based on the previous remarks, the main objective of the present work was the investigation of process performances when different multifunctional initiators were used to promote styrene free radical polymerizations at similar process conditions. Styrene polymerizations were carried out in solutions of ethylbenzene, according to the well-known process used for production of general purpose polystyrene (GPPS).<sup>36</sup> Polymerizations were conducted in batch at fixed concentrations of 95 wt % styrene and 5 wt % of ethylbenzene at high temperatures (120°C and 130°C) until conversions around 70%, as frequent in industrial sites. Polymerizations were conducted in glass test ampoules with different concentrations and types of initiators, parameterized in terms of the active oxygen concentration. Different multifunctional peroxide initiators were used (bi, tri, and tetrafunctional), and the observed performances were compared with the ones observed when polymerizations were initiated thermally or with a monofunctional initiator. Performances were compared in terms of monomer conversions and average molar masses of the obtained polymer material. Whenever possible, obtained results were compared with available published material.

It must be observed that real initiators do not necessarily present similar half-times at similar temperatures, especially when the temperature operation range must be defined beforehand for practical operation issues, as in many industrial processes. This is particularly true when one is concerned with multifunctional initiators, as the number of commercially available multifunctional peroxides is still small. Therefore, one is not free to select initiators that present similar half-times in a single specified temperature range. Besides, reaction temperatures can be changed at plant site, if necessary and advantageous for the

process operation. For example, in the analyzed case, the increase of reactor operation temperatures can be very useful if reduction of the molecular weight averages can be avoided by using multifunctional initiators. At higher temperatures monomer conversions (and reactor productivity) can be increased and solution viscosities can be reduced, improving the mixing characteristics of the continuous process. Therefore, parameterization of experimental results in terms of active oxygen concentration can be very useful for posterior analyses of available experimental data.

## EXPERIMENTAL

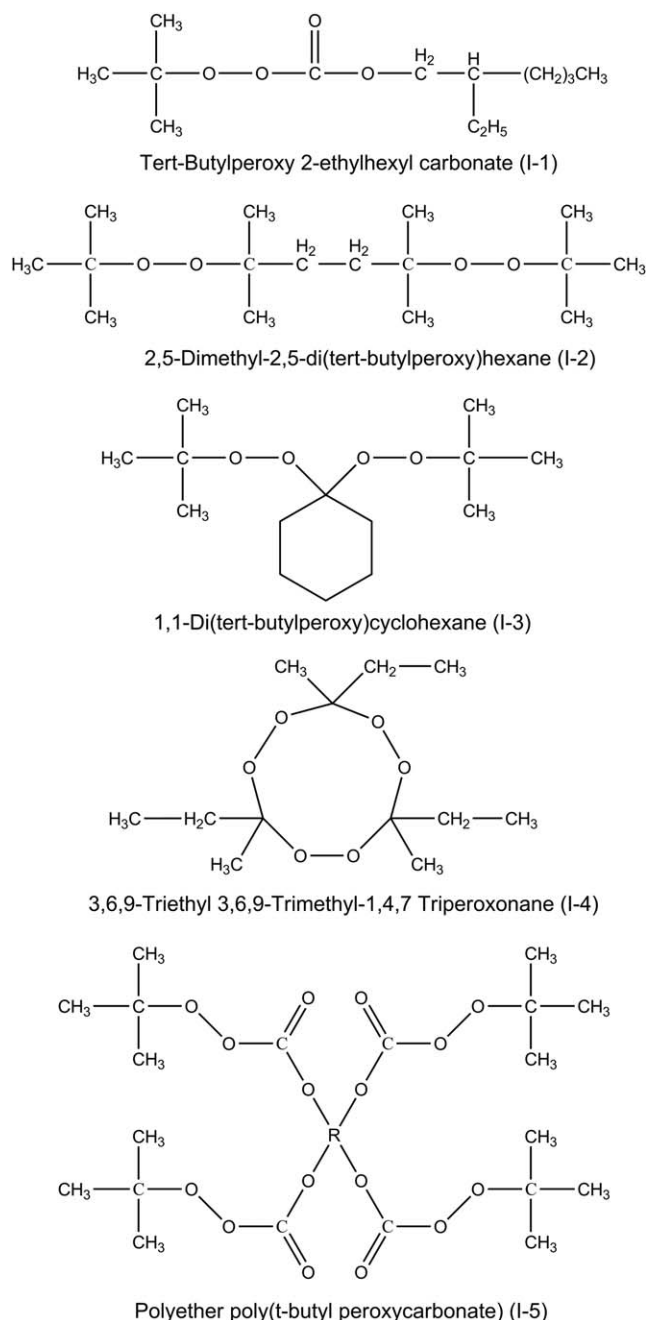
### Materials

All reagents were used as received, without further purification, as performed at plant site. The list of materials used to perform the polymerizations and characterize the obtained polymer resins is presented below.

- i. Styrene (monomer) supplied by Petrobras S.A. (Rio de Janeiro, RJ, Brazil) with minimum purity of 99.5 wt % and stabilized with 100 ppm of hydroquinone;
- ii. Ethylbenzene (solvent) supplied by Petrobras S.A. (Rio de Janeiro, RJ, Brazil) with minimum purity of 99.5 wt %;
- iii. Monofunctional initiator *tert*-butylperoxy 2-ethylhexyl carbonate supplied by Petrobras (Rio de Janeiro, RJ, Brazil), stabilized in oil and with concentration of 95 wt %;
- iv. Bifunctional initiator 2,5-dimethyl-2,5-di(*tert*-butylperoxy) hexane supplied by Petrobras (Rio de Janeiro, RJ, Brazil), stabilized in oil and with concentration of 92 wt %;
- v. Bifunctional initiator 1,1-di(*t*-butylperoxy)-cyclohexane supplied by Petrobras (Rio de Janeiro, RJ, Brazil), stabilized in oil and with concentration of 80 wt %;
- vi. Trifunctional initiator 3,6,9-triethyl 3,6,9-trimethyl-1,4,7 triperoxonane (Trigonox 301) supplied by Petrobras (Rio de Janeiro, RJ, Brazil), stabilized in oil and with concentration of 41 wt %;
- vii. Tetrafunctional initiator polyether tetrakis(*tert*butylperoxy carbonate) (Luperox JWEB50) supplied by Petrobras (Rio de Janeiro, RJ, Brazil), stabilized in oil and with concentration of 50 wt %;
- viii. Hydroquinone (inhibitor) supplied by VETEC (São Paulo, SP, Brazil), with minimum purity of 99 wt %;
- ix. Ethanol P.A. (solvent) supplied by VETEC (São Paulo, SP, Brazil), with minimum purity of 99.9 wt %;
- x. Tetrahydrofuran P.A. (THF, solvent used for GPC analyses) supplied by VETEC (São Paulo, SP, Brazil), with minimum purity of 99.9 wt %.

### Initiators

The chemical structures of all free-radical initiators used in the present work are presented in Figure 1. Table I shows the kinetic constants for rates of decomposition, half-life times, and active oxygen contents for each initiator. As initiators are usually commercialized in solution, to improve the stability during transportation and storage, active oxygen concentrations are shown in Table I both for the pure material and for the solution used in the present work. The active oxygen concentration can be calculated with the following equation:



**Figure 1.** Chemical structures of monofunctional (I-1), bifunctional (I-2 and I-3), trifunctional (I-4), and tetrafunctional (I-5) initiators used in the present work.

**Table I.** Main Properties of the Initiators Used in the Present Work (from AKZO<sup>37</sup> and ARKEMA<sup>38</sup>)

Initiator	$A_o$ ( $s^{-1}$ )	$E_a$ (kJ/mol)	$K_d$ (120°C) ( $s^{-1}$ )	Half-life times (min) at 120°C	Active oxygen pure (in oil), (mol %)
I-1	$4.07 \times 10^{16}$	151.72	$2.776 \times 10^{-4}$	42	6.49 (6.17)
I-2	$1.68 \times 10^{16}$	155.49	$3.614 \times 10^{-5}$	320	11.02 (10.14)
I-3	$3.47 \times 10^{15}$	142.40	$4.101 \times 10^{-4}$	30	12.29 (9.84)
I-4	$1.02 \times 10^{15}$	150.23	$1.098 \times 10^{-5}$	1053	18.16 (7.6)
I-5	$2.49 \times 10^{15}$	143.74	$1.953 \times 10^{-4}$	59	6.63 (3.45)

$$\%(\text{O}) = \frac{(\text{number of available O} - \text{O}) \times 16 \times 100}{\text{molecular weight}} \quad (1)$$

The active oxygen concentrations in solution were obtained from catalogs provided by the initiator manufacturers.<sup>37,38</sup>

### Reaction Procedure

Reactions were carried out in glass ampoules with a height of 10.0 cm and diameter of 5.0 mm. The ampoules were previously purged with nitrogen and degassed in vacuum chambers before addition of the reaction medium, performed in hoods with controlled atmosphere. The reacting medium was prepared by mixing the specified amounts of styrene (95 wt %) and ethylbenzene (5 wt %), inertization with nitrogen, and final addition of the specified amounts of initiator. After addition of the desired amounts (~10 mL) of the reacting mixture into the ampoules, the ampoules were sealed and placed simultaneously inside a bath (HAAKE Phoenix II P1-C35P) filled with silicone fluid 200/350CST and kept at the desired reaction temperature. A thermocouple (K-type) was inserted into the ampoule in all experiments, and no significant temperature rise was ever observed because of the small volume occupied (~10 mL) by the reactants inside the ampoules. At specified sampling times, ampoules were removed from the thermostatic bath, cooled quickly in cold water, and opened. A solution of hydroquinone in ethanol (1.0 wt %) was added into the ampoule to interrupt the polymerization and force the precipitation of polystyrene. The ampoules were then dried in a vacuum oven at 30°C for 24 hours until constant weight. Table II summarizes the reaction conditions used to perform the experiments.

### Characterization

Monomer conversions were obtained gravimetrically by careful weighing of dry ampoules before and after the reaction experiments.

Averages molar masses ( $\overline{M}_m$ ) and molar mass distributions (MMD) were determined for each dry polymer sample with help of a Viscotek VE2001 chromatograph equipped with four Phenomenex columns and Refractometric Detector Viscotek VE3580. PS standards with molar masses ranging from 500 to  $1.85 \times 10^6$  g/mol were used for calibration. Analyses were conducted at 40°C using tetrahydrofuran (THF) as the mobile phase.

## RESULTS AND DISCUSSION

### Thermal Polymerization

Thermal styrene polymerizations, performed in absence of initiators, constitute important benchmarks for the present study. Several published works investigate the thermal bulk polymerization of styrene.<sup>13,39–41</sup> Particularly, Walling *et al.*<sup>42</sup> investigated the

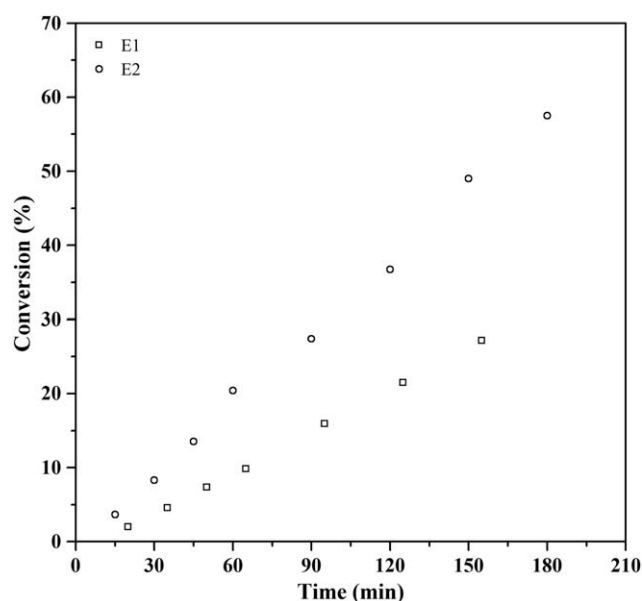
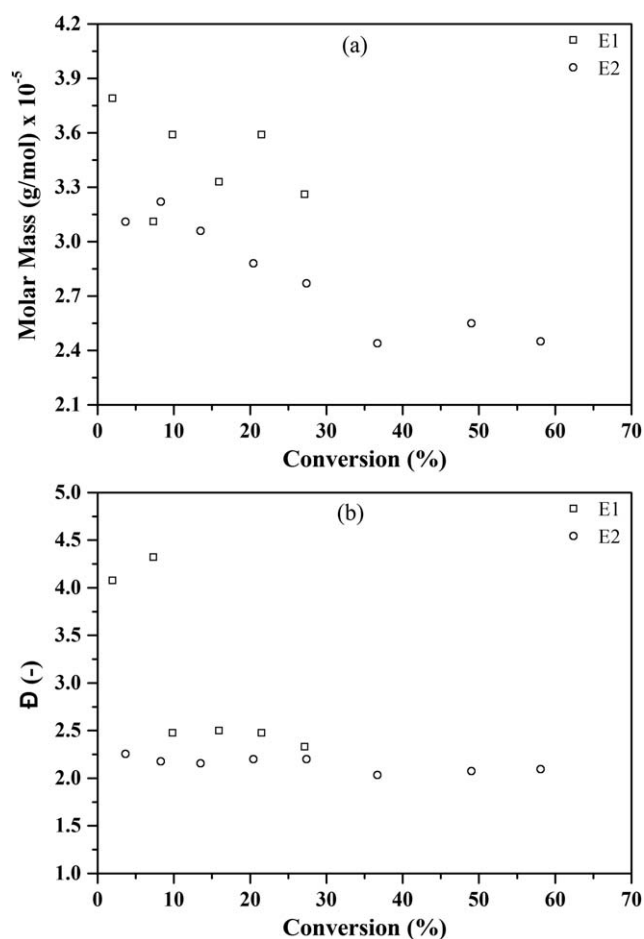
**Table II.** Experimental Conditions

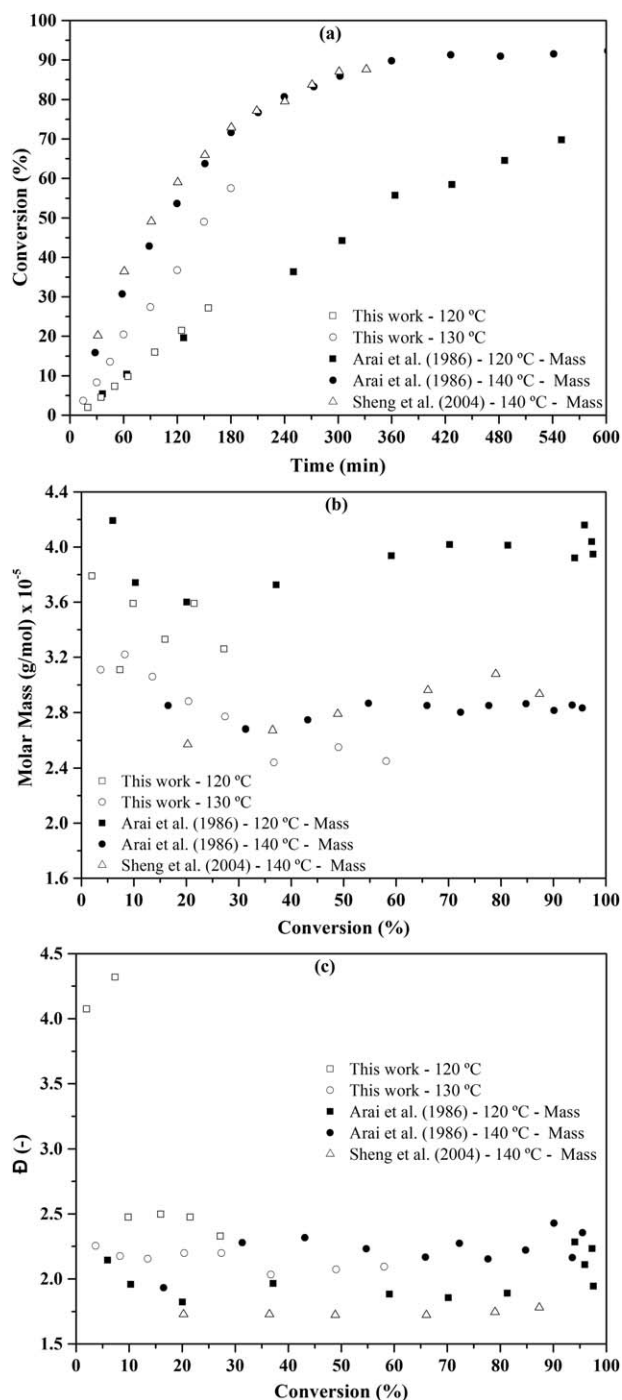
Experiment	Initiator	Trade name	Type	T (°C)	[I] (mmol/L)
E1	-	-	-	120	-
E2	-	-	-	130	-
E3	tert-Butylperoxy 2-ethyl carbonate	Luperox TBEC/Trigonox 117	Mono	120	1.3 ± 0.1
E4	tert-Butylperoxy 2-ethyl carbonate	Luperox TBEC/Trigonox 117	Mono	120	2.5 ± 0.1
E5	2,5-Dimethyl 2,5-di(tert-butylperoxy) hexane	Luperox 101/Trigonox 101	Bi	120	0.75 ± 0.1
E6	1,1-di(tert-Butylperoxy) cyclohexane	Luperox 331/Trigonox 22	Bi	120	1.2 ± 0.1
E7	1,1-di(tert-Butylperoxy) cyclohexane	Luperox 331/Trigonox 22	Bi	120	1.8 ± 0.1
E8	3,6,9-Triethyl 3,6,9-trimethyl-1,4,7 triperoxonane	Trigonox 301	Tri	120	0.75 ± 0.1
E9	Polyether poly(t-butyl peroxy carbonate)	Luperox JWEB	Tetra	120	0.38 ± 0.1
E10	Polyether poly(t-butyl peroxy carbonate)	Luperox JWEB	Tetra	130	0.40 ± 0.1

thermal styrene polymerizations is similar ranges of reaction temperatures and found that the monomer conversion followed an almost linear profile throughout the process. However, as the open literature does not provide data regarding the thermal polymerization of styrene in solutions of ethylbenzene at the conditions shown in Table II, experiments were carried out for comparative purposes at 120°C (E1) and 130°C (E2). Monomer conversions, average molar masses, and dispersity ( $\bar{D}$ ) results are shown in Figures 2 and 3(a,b), respectively.

As expected, reaction rates are higher and average molar masses are lower at higher temperatures. The characteristic linear increase of monomer conversions in thermal styrene polymerizations is related to the mild gel effect of styrene polymerizations.<sup>35,36</sup> The increase of monomer conversion with temperature is related to the increase of rates of thermal initiation and propagation.<sup>9,10</sup> The decrease of the average molar masses with the temperature increase is related to the faster

increase of rates of chain termination, when compared with the rates of propagation. The gradual decrease of average molar masses with time is related to the decreasing monomer concentration during the reaction evolution. The final dispersity results were always close to 2, as expected for chain termination controlled by disproportionation and transfer to a chain transfer

**Figure 2.** Conversion data for experiments E1 and E2.**Figure 3.** Weight-average molar masses and dispersity results as functions of monomer conversion for experiments E1 and E2.



**Figure 4.** Comparison of obtained experimental data with published data for thermal styrene polymerizations. (a) Conversion  $\times$  time; (b) weight-average molar masses  $\times$  conversion; and (c)  $D \times$  conversion.

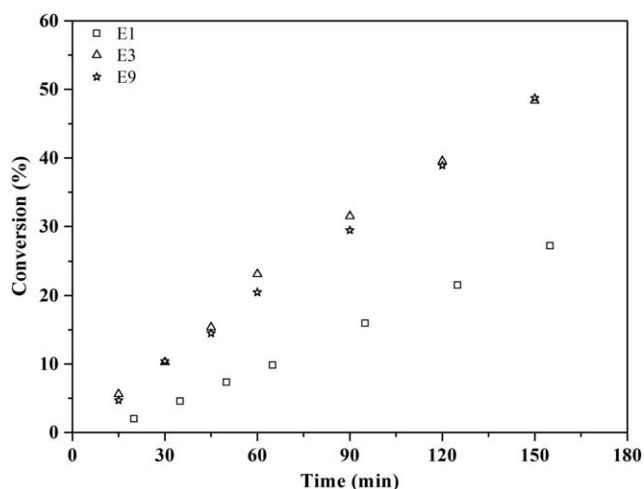
agent. As chain termination in styrene polymerizations is controlled by chain combination, the dispersity values reflect the variation of the average molar masses along the reaction trajectory.<sup>9,10,35,36</sup> It must be observed that obtained molecular weight distributions are not shown here because they presented the usual monomodal shape of polystyrene materials prepared through free-radical polymerizations in all analyzed cases.

The obtained data were compared with the data presented by Arai *et al.*<sup>41</sup> and Sheng *et al.*<sup>13</sup> for bulk styrene polymerizations, as shown in Figure 4, and results can be regarded as very similar. This is not surprising, given the low amounts of ethylbenzene used in the experiments. Anyway, it becomes clear that the presence of ethylbenzene in the reacting medium exerts little influence on the reaction course.

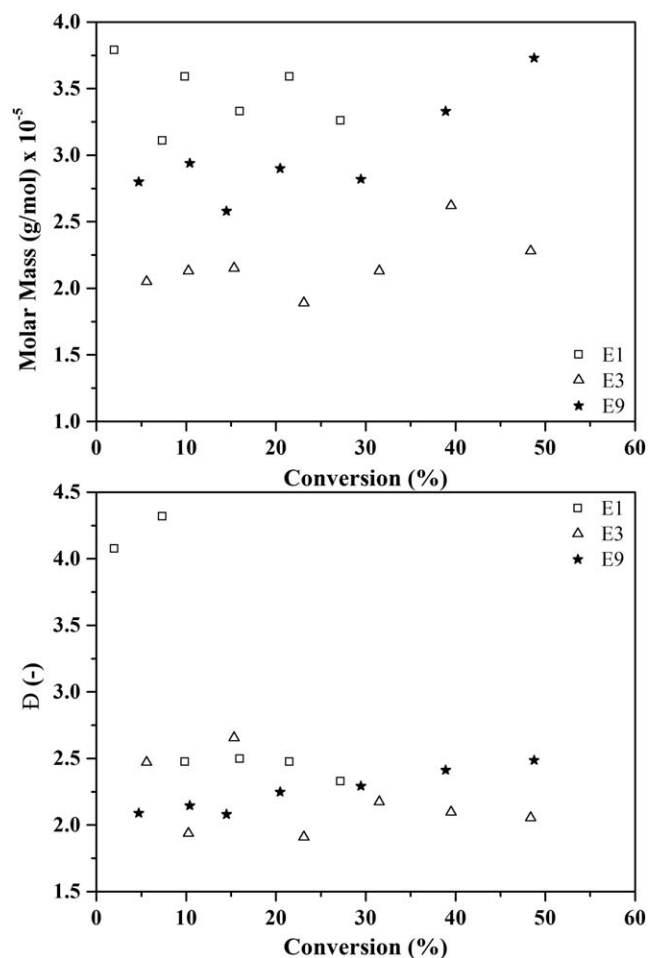
### Monofunctional VS Tetrafunctional

The comparison between the performances of monofunctional and tetrafunctional initiators was investigated in several papers published by Penlidis and coworkers for different bulk polymerization systems,<sup>7,8</sup> although not in the conditions of interest presented in Table II. In one of their works, Penlidis and coworkers<sup>7</sup> show that for the homopolymerization of styrene, JW50 produced polymer molecular weights similar to TBEC at the same concentration. In the present work, the performances obtained with the tetrafunctional initiator (I-5) were compared with the performances obtained with the monofunctional initiator (I-1) and also with the thermal initiation. For both I-1 and I-5, the concentrations of peroxide groups were kept constant (monofunctional initiator concentration of 1.3 mmol/L tetrafunctional initiator concentration of 0.38 mmol/L).

Figure 5 shows monomer conversions for reactions E1, E3, and E9. Figure 5 shows clearly that the presence of the initiator led to increase of the reaction rates (because of the production of additional amounts of free radicals through initiator decomposition), although the characteristic linear profile remained (because of the mild gel effect of styrene polymerizations). It is important to observe that trajectories of monomer conversions for experiments E3 and E9 were essentially the same, given the equal concentrations of active oxygen and the similar half-life times, as shown in Table I. Based on these results, it seems plausible to assume that the decomposition of one peroxide group of the tetrafunctional initiator did not affect the rates of decomposition of the remaining ones, as the reaction proceeded as initiated by a monofunctional initiator. Therefore, as also discussed by Fityani-Trimmi *et al.*,<sup>28</sup> the relative proportions of initiator concentrations (I-1/I-5) should be based on the active



**Figure 5.** Conversion data for experiments E1, E3, and E9.



**Figure 6.** Weight-average molar masses and dispersity results as functions of monomer conversion for experiments E1, E3, and E9.

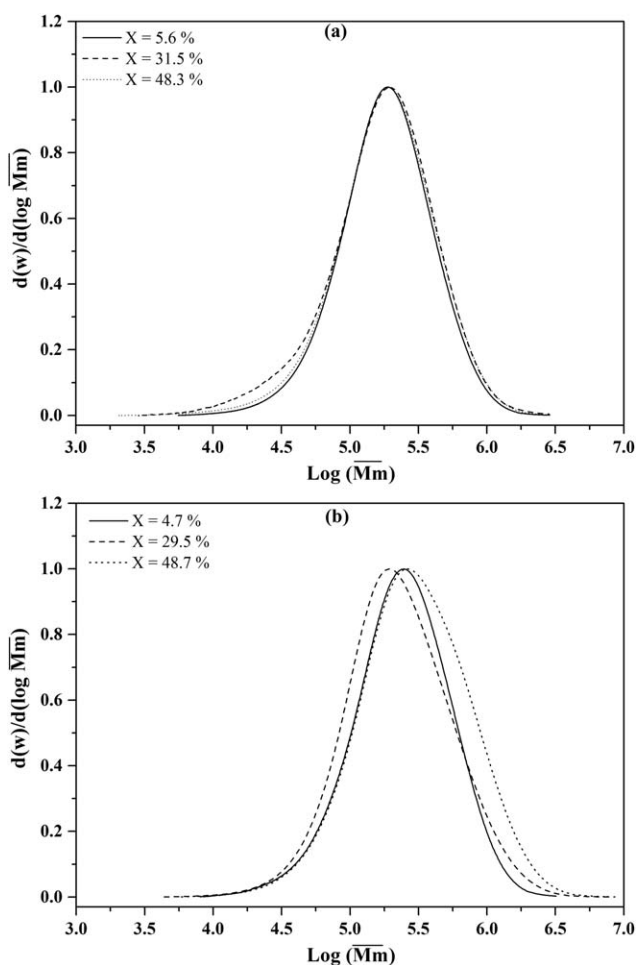
oxygen concentrations and not simply on the proportions suggested by the molecular structures (in the present case, 3.67 instead of 4), as often assumed in the literature.<sup>7,8,28</sup>

Figure 6 shows the average molar masses and dispersity results for experiments E1, E3, and E9. Higher average molar masses were obtained for the thermal polymerization (E1) because of the much lower concentrations of free-radicals, when compared with reactions performed with the addition of initiator. However, when one analyzes the performances obtained with initiators I-1 and I-5, it can be observed that addition of the tetrafunctional initiator led to polymer products with higher average molar masses and dispersities. This is certainly related to the decomposition of multiple peroxide groups of the initiator molecule, which can lead to chain growth in multiple directions and to formation of branched polymer chains.<sup>8</sup> Therefore, Figure 6 shows clearly that the use of the tetrafunctional initiator can lead to polymer materials with different molecular properties at similar reaction rates, when compared with the monofunctional initiator. This result could already be expected because of the tetrafunctional nature of initiator I-5.

Figure 7 shows the evolution of the molar mass distributions of the polymer products obtained with initiators I-1 and I-5.

Although one cannot see the development of a distinct second mode in the MMDs, widening of the MMD becomes obvious when initiator I-5 was used, with the formation of a population of polymer chains with very large molar masses. Although not unequivocal, this result provides indirect evidence of production of branched polymer material with initiator JWEB, as already discussed in the literature.<sup>29</sup> Besides, the continuous increase of the average molar mass with conversion when the initiator I-5 was used is because of the gradual decomposition of the multiple peroxide groups of JWEB. As the peroxide groups do not decompose simultaneously, the molar mass of the multifunctional polymer chains grow slowly with conversion, as the number of decomposed peroxide groups increase. This also explains why average molar masses obtained with the monofunctional initiator change much less significantly with monomer conversion.

The obtained data were compared with the data presented by Scoriah *et al.*<sup>8</sup> for bulk styrene polymerizations. Reaction conditions are shown in Table III. Monomer conversions, average molar masses, and dispersity values are shown in Figure 8. Scoriah *et al.*<sup>8</sup> carried out the experiments at lower temperatures (110°C) and used initiator concentrations that were ten times larger than the ones used in the present work. Surprisingly,



**Figure 7.** Evolution of the molar mass distribution of PS. (a) Experiment E3 (TBEC) and (b) experiment E9 (JWEB).

**Table III.** Experimental Conditions Used in the Present Work and Used by Scoria *et al.* (2006)<sup>8</sup>

	[I-1] (mmol/L) monofunctional	[I-5] (mmol/L) tetrafunctional	T (°C)	Process
Scoria <i>et al.</i> (2006)	16.0	-	110	Mass
Scoria <i>et al.</i> (2006)	-	4.0	110	Mass
This work	1.3 (E3)	-	120	Solution (5 wt % ethylbenzene)
This work	-	0.38 (E9)	120	Solution (5 wt % ethylbenzene)

experimental monomer conversions were very similar in all cases, which cannot be explained only in terms of initiation rates, as shown in Table I. However, Scoria *et al.*<sup>8</sup> reported much lower dispersities than reported in the present manuscript, which cannot be explained in terms of the classical free-radical polymerization mechanism and can possibly indicate the occurrence of more complex reaction kinetics. Based on Figure 8, it can be assumed that small changes of the operation conditions can exert pronounced effects on the reaction mechanism in presence of different initiators, reinforcing the argument presented previously that comparisons must be performed at similar conditions.

#### Monofunctional VS Bifunctional

In this section, the performances obtained with a bifunctional initiator (I-3) were compared with the performances obtained with the monofunctional initiator (I-1) and with the thermal initiation. It must be mentioned that data for styrene polymerizations initiated by 1,1-di(*tert*-butylperoxy) cyclohexane (I-3) have not been found in the open literature.

Figure 8 shows monomer conversions obtained for reactions initiated thermally and with mono- and bifunctional initiators. Figure 9 shows once more that the presence of the initiator led to increase of the reaction rates (because of the production of additional amounts of free radicals through initiator decomposition), although the characteristic linear profile remained (because of the mild gel effect of styrene polymerizations). It is important to observe that trajectories of monomer conversions for experiments E3 and E6 were essentially the same, given the equal concentrations of active oxygen and the similar half-life times, as shown in Table I. Based on these results, it seems plausible to assume that the decomposition of one peroxide group of the bifunctional initiator did not affect significantly the rates of decomposition of the remaining one, as reaction proceeded as initiated by a monofunctional initiator (although the slope of the reaction rate is slightly different for the bifunctional initiator). As expected, the increase of the initiator concentration led to higher reaction rates.

Figure 10 shows the average molar masses and dispersity results for experiments E1, E3, E4, and E6. It must be observed that obtained molecular weight distributions are not shown here because they presented the usual monomodal shape of polystyrene materials prepared through free-radical polymerizations in all analyzed cases. Higher average molar masses were obtained once for the thermal polymerization (E1) because of the much lower concentrations of free-radicals, when compared with reactions performed with the addition of initiator. However, when

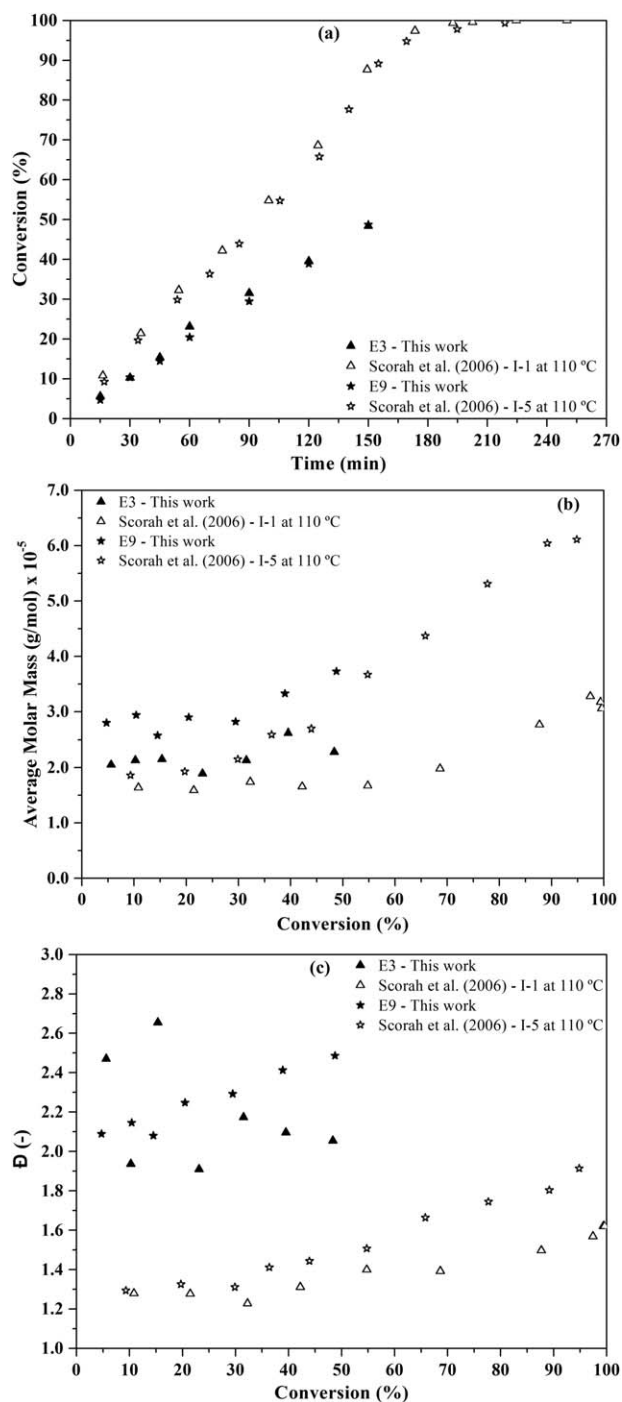
one analyzes the performances obtained with initiators I-1 and I-3, it can be observed that addition of the bifunctional initiator led to polymer products with higher average molar masses and dispersities, although differences were less significant than observed previously for the tetrafunctional initiator. This is certainly related to the decomposition of multiple peroxide groups of the initiator molecule, which can lead to chain growth in multiple directions and to formation of branched polymer chains, as already explained.<sup>8</sup> Therefore, Figure 9 shows once more that the use of the bifunctional initiator can lead to polymer materials with different molecular properties at similar reaction rates, when compared with the monofunctional initiator.

It is important to observe in Table I that the half-life times of initiators I-1 and I-3 are relatively small (around 30 minutes) when compared with the characteristic reaction times of the reaction (~4 hours), indicating that reaction is initially dominated by the decomposition of the initiator and then dominated by thermal initiation after 1–2 hours of reaction. This can explain the small differences observed in the average molar masses of the final products and can justify the use of cocktails of initiators for real commercial runs.

#### Bifunctional VS Trifunctional

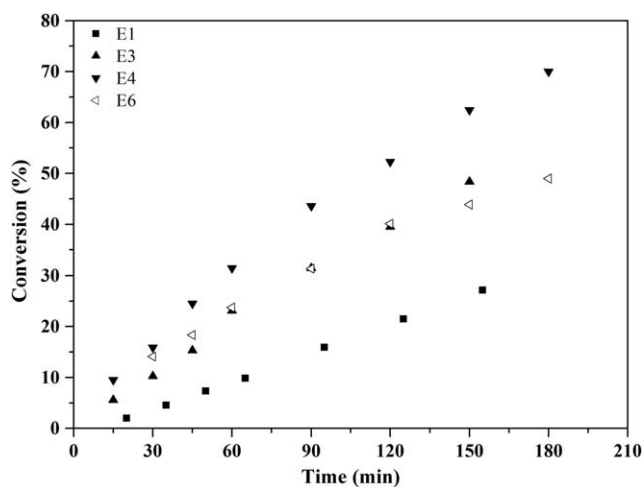
In this section, the performances obtained with a bifunctional initiator (I-2) were compared with the performances obtained with the trifunctional initiator (I-4) and also with the thermal initiation. It is worth mentioning that the initiator 2,5-dimethyl 2,5-di(*tert*-butylperoxy) hexane (I-2) has been used in several research studies to modify the properties of polyethylene<sup>43</sup> and polypropylene<sup>44,45</sup> grades and to promote the grafting of maleic anhydride onto poly(lactic acid) (PLA)<sup>46</sup>. However, data for styrene polymerizations initiated by 2,5-dimethyl 2,5-di(*tert*-butylperoxy) hexane (I-2) have not been found in the open literature. The bifunctional initiator I-2 was selected to compare initiators with more similar thermal decomposition rate constants, as illustrated in Table I.

Figure 11 shows monomer conversions obtained for reactions initiated thermally (E1) and with the analyzed bi- (E5) and trifunctional (E8) initiators. Figure 12 shows the average molar masses and dispersity results for experiments E1, E5, and E8. Figures 11 and 12 show that the results were very similar in all cases, indicating the predominant control of thermal initiation, which is fully compatible with the half-life times presented in Table I. From a practical point of view, it can be difficult to justify the use of these initiators at plant site, unless it is intended to operate the reactor at much higher temperatures. Despite that, Sheng *et al.*<sup>13</sup> studied the bulk polymerization of styrene at



**Figure 8.** Comparison of obtained experimental data with published data for styrene polymerizations performed with different initiators. (a) Conversion  $\times$  time; (b) Weight-average molar masses  $\times$  conversion; and (c)  $\bar{D}$   $\times$  conversion.

120 °C with initiator I-4 using initiator concentrations 6.6 times higher than used in the present work. However, according to Figure 13, results obtained by Sheng *et al.*<sup>13</sup> were not much different from the ones presented here, which can certainly be explained by the half-life times presented in Table I. Nevertheless, Sheng *et al.*<sup>13</sup> reported the slow and continuous increase of the average molar masses, which can be explained in terms of

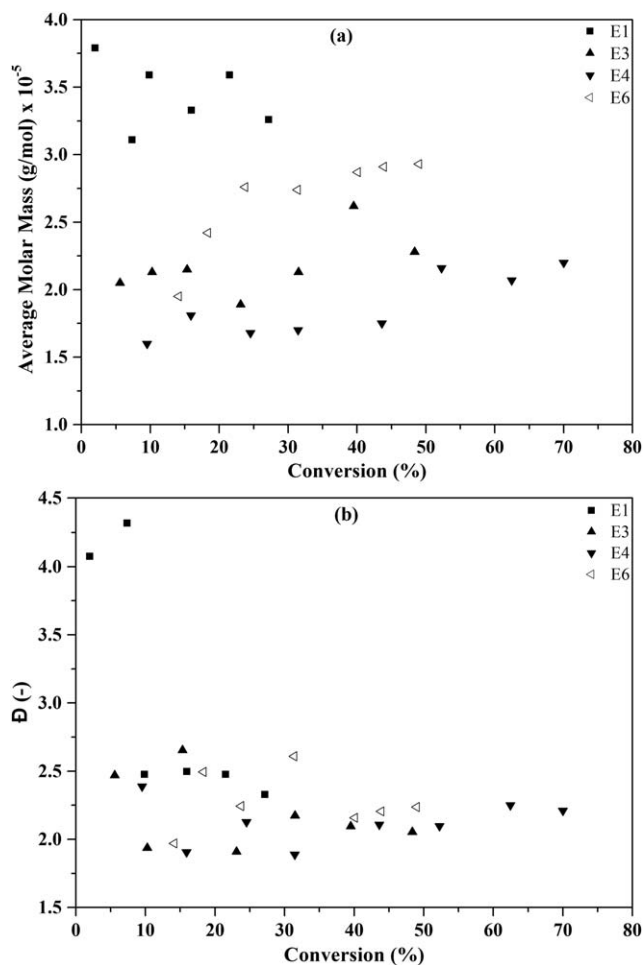


**Figure 9.** Conversion data for experiments E1, E3, E4, and E6.

the very slow decomposition of fragments of the initiator molecule incorporated into the polymer chains.

### Trifunctional VS Tetrafunctional

In this section, the performances obtained with a trifunctional initiator (I-4) were compared with the performances obtained



**Figure 10.** Weight-average molar masses and dispersity results as functions of monomer conversion for experiments E1, E3, E4, and E6.



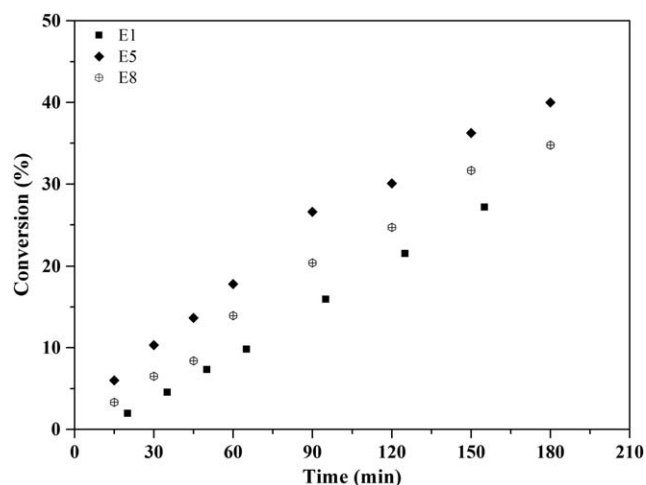


Figure 11. Conversion data for experiments E1, E5, and E8.

with the tetrafunctional initiator (I-5) and also with the thermal initiation. Figure 14 shows monomer conversions obtained for reactions initiated thermally (E1) and with the analyzed tri- (E8) and tetrafunctional (E9) initiators. Figure 15 shows the average molar masses and dispersity results for experiments E1,

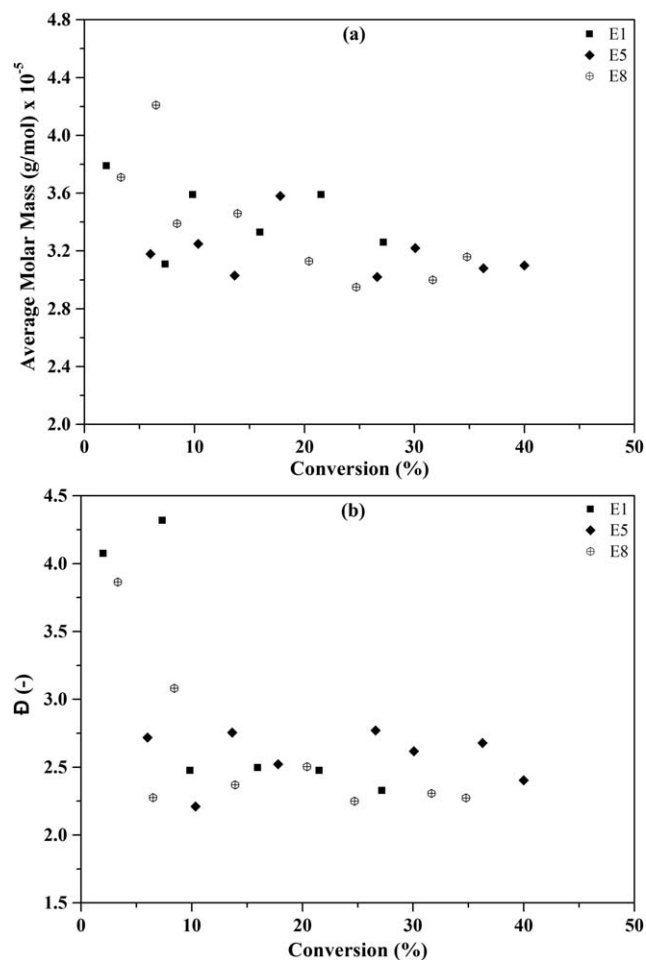


Figure 12. Weight-average molar masses and dispersity results as functions of monomer conversion for experiments E1, E5, and E8.

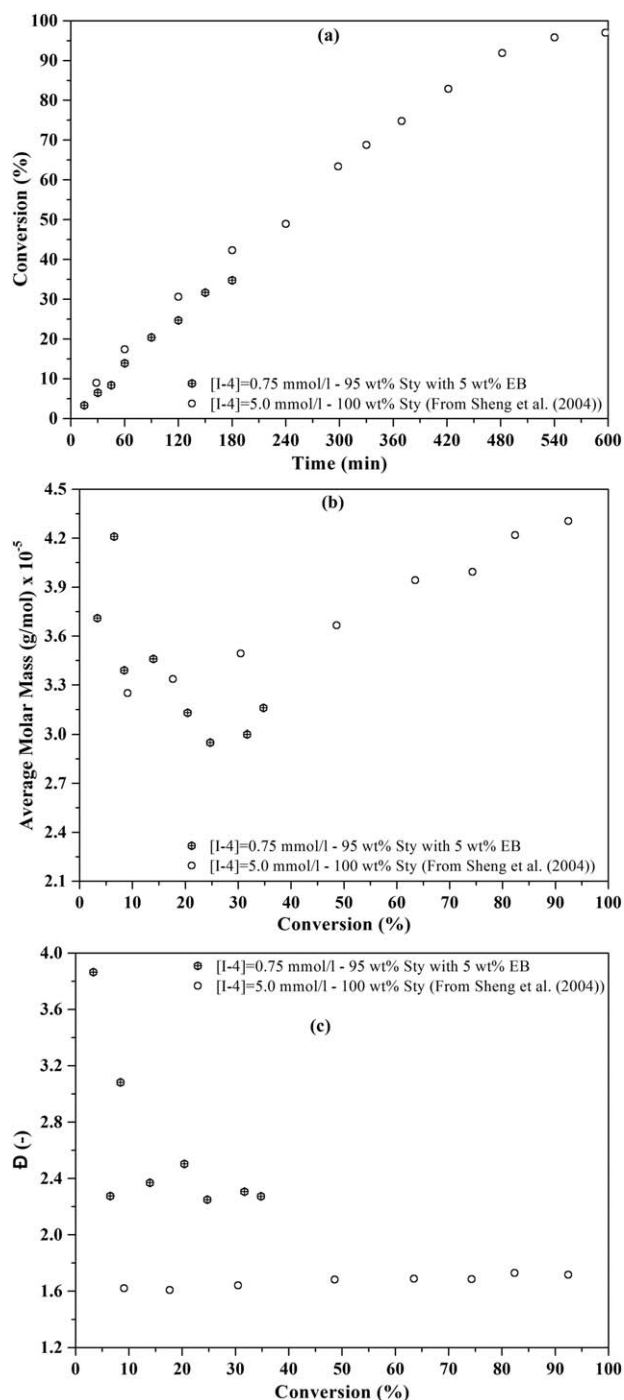


Figure 13. Comparison of obtained experimental data with published data for styrene polymerizations performed with a trifunctional initiator. (a) Conversion  $\times$  time; (b) Weight-average molar masses  $\times$  conversion; and (c)  $D \times$  conversion.

E8, and E9. It must be observed that obtained molecular weight distributions are not shown here because they presented the usual monomodal shape of polystyrene materials prepared through free-radical polymerizations in all analyzed cases. Obtained results were very similar to the ones presented in Figures 5 and 6 because of the low thermal decomposition rate constants of the trifunctional initiator. From a pragmatic point

of view, there is no doubt that the use of the analyzed tetrafunctional initiator allows for much higher flexibility at plant site at the analyzed process conditions, leading to products with higher average molar masses with higher reaction rates. To lead to decomposition rates that are similar to the decomposition rate of the tetrafunctional initiator at 120°C, according to Table I the trifunctional initiator should be employed at 150°C, which can be regarded as too high for styrene polymerizations. Alternatively, the initiator concentrations might be multiplied by 10, in the case of the trifunctional initiator, although this would certainly cause problems for the process economics and possibly perturb the final product stability (as polymer chains might contain significant amounts of unreacted peroxide groups).

## CONCLUSIONS

This paper analyzed the performance of multifunctional initiators frequently used in the literature and in the industry for production of polystyrene (PS) on a similar ground for the first time. The analyzed initiators were *tert*-butylperoxy 2-ethylhexyl carbonate, 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane, 1,1-di(*t*-butylperoxy)-cyclohexane, 3,6,9-triethyl 3,6,9-trimethyl-1,4,7 triperoxonane and tetrakis(*tert*butylperoxy carbonate). The bifunctional initiators 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane and 1,1-di(*t*-butylperoxy)-cyclohexane were used to perform bulk styrene polymerizations for the first time.

Polymerizations of styrene (95 wt %) in ethylbenzene (5 wt %) were conducted in batch at high temperatures (120°C) until conversions around 70%, as frequent in industrial sites for production of general purpose polystyrene (GPPS) resins. Polymerizations were conducted in glass test ampoules with different concentrations and types of initiators, parameterized in terms of the active oxygen concentration.

The results showed that when used at similar active oxygen concentrations, the use of the tetrafunctional initiator polyether tetrakis(*tert*butylperoxy carbonate) can allow for production of polymer resins with significantly higher average molar masses and with similar polymerization rates when compared with the bifunctional initiator 1,1-di(*t*-butylperoxy)-cyclohexane, which

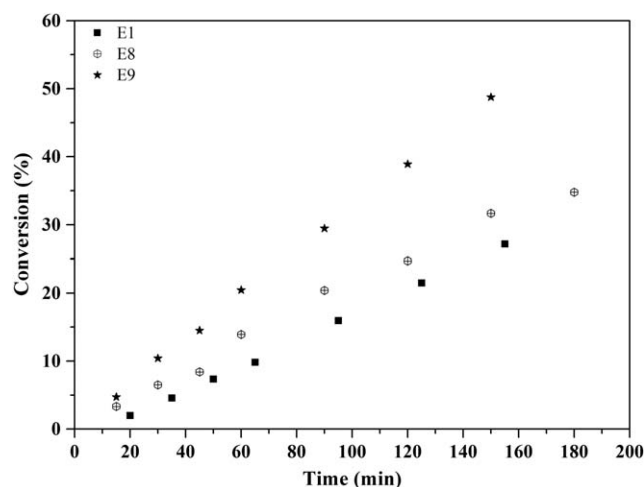


Figure 14. Conversion data for experiments E1, E8, and E9.

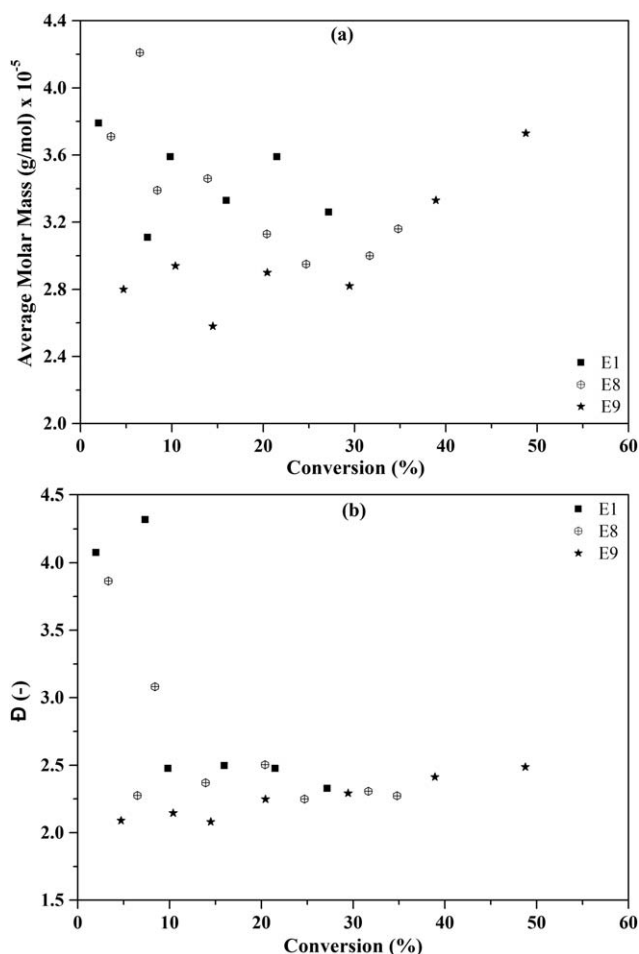


Figure 15. Weight-average molar masses and dispersity results as functions of monomer conversion for experiments E1, E8, and E9.

can be very useful at plant site for modification of polymer grades. Besides, the results show that the decomposition of one peroxide group of the analyzed multifunctional initiators did not affect the rates of decomposition of the remaining peroxide groups significantly, as the reaction proceeded as initiated by a monofunctional initiator.

Finally, although described in previous styrene polymerization studies, the use of the trifunctional initiator 3,6,9-triethyl 3,6,9-trimethyl-1,4,7 triperoxonane is difficult to justify in commercial units at the analyzed conditions, given its very high half-life time and dynamic trajectories that resemble the ones obtained with the thermal initiation. To be effective and lead to results that are comparable to the one obtained with the tetrafunctional initiator, the reaction temperatures should be around 150°C, generally regarded as too high for styrene polymerizations.

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