

# Living Free Radical Polymerization Using Cyclic Trifunctional Initiator

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**ABSTRACT:** Free radical polymerization is a very robust route to produce polymers, however, it does not promote a control on the microstructure of the polymer: usually polymers with wide molecular weight distribution and polydispersity (PDI) greater than 1.5 are obtained. Ionic polymerization can be used to produce polymers with low PDI, however, this kind of route needs to be held with a high degree of purity. Living free radical polymerization (LFRP) is a promising technique to produce controlled polymers. In the literature, monofunctional conventional initiators have been used in LFRP process. In this study, the use of a cyclic trifunctional peroxide on controlled nitroxide mediated radical polymerization was investigated. The initiator used was

Trigonox 301 (3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane—41% solution in isoparaffinic hydrocarbons) and TEMPO (2,2,6,6-tetramethyl-1-piperidin-1-oxyl) was used as controller agent. The results obtained show that it is possible to produce controlled polymers at certain operating conditions, when Trigonox 301 is used. It could be observed that the concentration of initiator and the ratio [TEMPO]/[Trigonox 301] have a huge effect on the polymer properties. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3900–3904, 2012

**Key words:** living free radical polymerization; polymer synthesis; trifunctional initiator; 2,2,6,6-tetramethyl-1-piperidin-1-oxyl

## INTRODUCTION

Living free radical polymerization (LFRP) is a process that involves the addition of a capture agent able to promote a reversible reaction of activation–deactivation in growing chains. There are different manners to perform LFRP and nitroxide mediated radical polymerization (NMRP) technique uses a stable nitroxide radical to promote the activation–deactivation reaction. This reversible reaction, however, reduces the polymerization rate, making the process slower. When dealing with standard polymerization, several studies show the application of initiators with functionality greater than one to accelerate the reaction rate, keeping the polymer properties. Most of them use bifunctional initiators.<sup>1–7</sup> On the same hand, Dias et al.<sup>8</sup> proved that it is possible to increase the velocity of NMRP reaction without causing significative changes on molecular weight, if bifunctional initiator is used.

Cerna et al.<sup>9</sup> reported a study of cyclic trifunctional initiator on conventional polymerization. They showed that depending on the temperature adopted, the initiator can follow different pathways of dissoci-

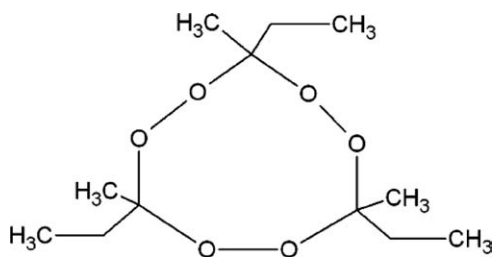
ation, promoting alterations on polymerization process. For example, a cyclic trifunctional initiator can have all its three bonds ruptured at the beginning of the process, releasing consequently a higher number of free radicals, or can gradually decompose each one of their label groups, as the reaction occurs. The authors prove that under specific experimental conditions narrow molecular weight distributions (MWDs) and polydispersities (PDIs) around 1.5 can be obtained. Scoria et al.<sup>10</sup> used a tetrafunctional initiator on conventional polymerization and proved that it is possible to produce polymers with different structures when compared to the ones produced using monofunctional initiator. Zhang and Zhang<sup>11</sup> produced a star copolymer of styrene and butadiene using a multifunctional macromolecular initiator.

One potential advantage on using trifunctional or tetrafunctional initiator on conventional polymerization is the possibility of generating more branches on the chains. Cyclic structure can also contribute for branch formation. Tetrafunctional initiator generates polymers with star chemical structure, which can be desired in some cases.

There are some papers in the literature reporting the use of initiators with functionality bigger than one when dealing with atom transfer radical polymerization (ATRP) process.<sup>12–14</sup> There are also some papers in the literature using NMRP process with different chemical structures of initiators or different alkoxyamines.<sup>15–17</sup> However, works dealing with

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**Figure 1** Chemical structure of the initiator Trigonox 301.

NMRP process and initiator with functionality bigger than one are scarcer in the literature and most of them work with bifunctional initiator, as can be seen in Dias et al.<sup>8</sup> As long as we know, there is no work published dealing with NMRP processes and cyclic trifunctional initiator. Therefore, the work showed in this article brings an important contribution toward a better comprehension on how structural aspects of the initiator and controller can influence the final characteristics of the synthesized polymers.

In this work, a cyclic trifunctional initiator Trigonox 301, which contains three bonds oxygen–oxygen in its chemical structure, is used in NMRP process. The chemical structure of the initiator Trigonox 301 is shown in Figure 1.

## EXPERIMENTAL

The monomer styrene (Sigma–Aldrich, São Paulo, Brazil, purity  $\geq 99\%$ , Reagent Plus, CAS Number: 100-42-5) was washed three times with 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. After that desired quantities of monomer (styrene), initiator (Trigonox 301—CAS Number: 24748-23-0, provided by Akzo Nobel Polymer Chemicals), and controller 2,2,6,6-tetramethyl-1-piperidin-1-oxyl (TEMPO; Aldrich Chemistry, cat.: 21.400-0, C<sub>9</sub>H<sub>18</sub>NO, CAS Number: 2564-83-2, purity  $\geq 98\%$ ) were weighed, added in beakers, and transferred to glass ampoules. The ampoules were degassed by three cycles of freezing and thawing under vacuum. Each ampoule was sealed using a torch of fire. The ampoules were placed in a bath of oil at a certain temperature, where polymerization occurs. The ampoules were withdrawn at various pre-established intervals of time, 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

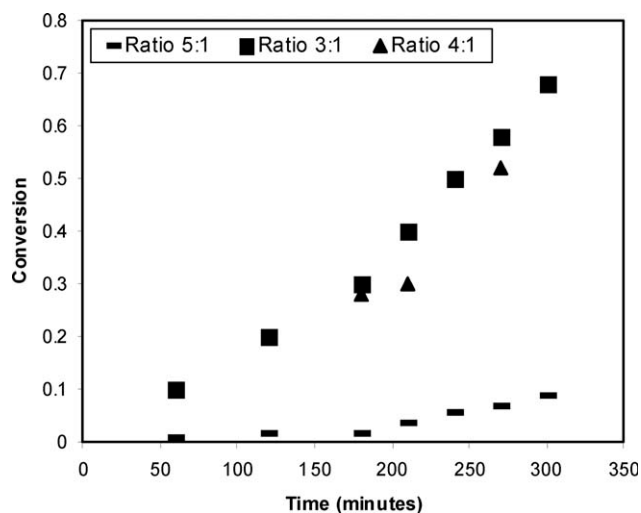
for analysis in a GPC (gel permeation chromatography—Malvern) with a triple detector: refraction index, viscosimeter, and right-angle laser light scattering. The GPC used presents two columns of separation ViscoGel (I—MBHMW 3078), automatic sampler (GPCmax—Viscotek), and a module TDA Viscotek 302 (which contains a furnace for the two columns of separation). The temperature of the furnace is 40°C, and the mobile phase tetrahydrofuran (THF) flow rate is 1.0 mL/min.

## RESULTS AND DISCUSSION

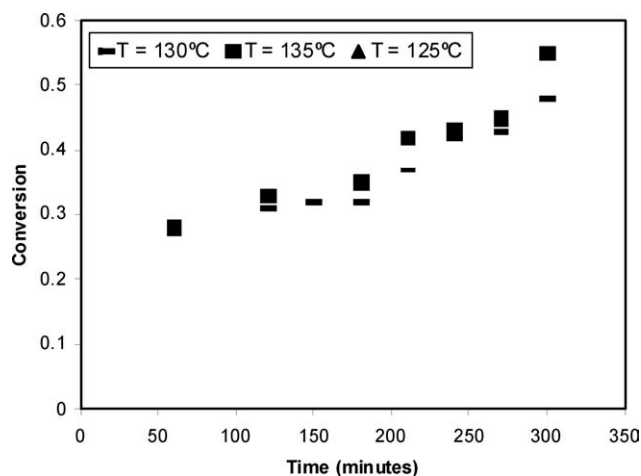
It is known that the balance between radicals and nitroxide species is very important for controlled polymerization. When monofunctional initiator is used, only the initiator efficiency should be considered, and the ratio between controller and initiator adopted is usually 1.1–1.3.<sup>18–20</sup> When bifunctional or multifunctional initiator is used, the nonhomogeneous breaking of the different peroxide groups has also to be taken into account.

Keeping this in mind, in this work, three different ratios [controller]/[initiator] were studied: 5 : 1, 4 : 1, and 3 : 1. In a first attempt, initiator concentration equal to 0.0029 mol/L and temperature of 125°C were considered.

Conversion profiles can be seen in Figure 2, when the three different ratios [TEMPO]/[Trigonox 301] were used. When using ratio 5 : 1, the reaction rate is very slow. Even if all peroxide groups of the Trigonox 301 were broken at the same time, 1 mol of initiator would generate 6 mol of radicals. Taking into account the initiator efficiency, it seems that in the ratio 5 : 1 there is an excess of controller, making the reaction very slow. Figure 2 also shows that ratios



**Figure 2** Conversion versus time profile at three different ratios [TEMPO]/[Trigonox 301].  $T = 125^{\circ}\text{C}$ , [Trigonox] = 0.0029 mol/L.

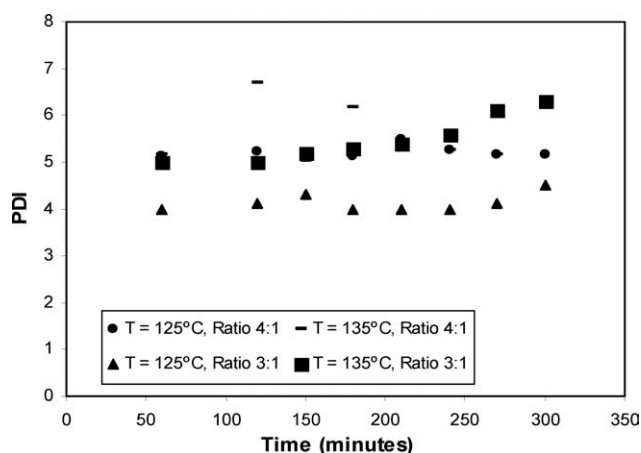


**Figure 3** Conversion versus time profile for three different temperatures. Ratio [TEMPO]/[Trigonox 301] = 4 : 1, [Trigonox 301] = 0.0029 mol/L.

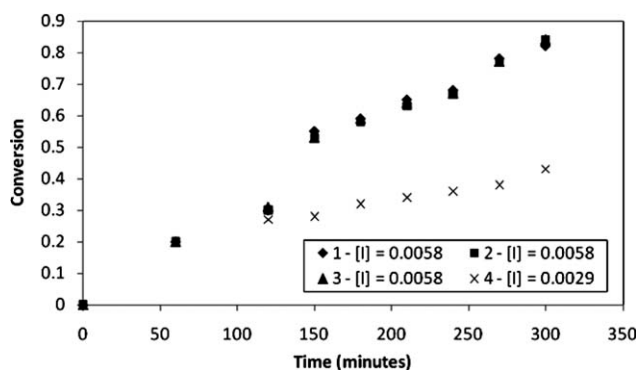
3 : 1 and 4 : 1 present similar conversion profiles. In this way, only ratios 3 : 1 and 4 : 1 will be considered from now on.

On the same hand, Figure 3 shows the effect of temperature on conversion profile, when the ratio controller/initiator is equal to 4 : 1. Similar behavior is obtained, when ratio 3 : 1 is used. Observing Figure 3, we can realize that for all the three temperatures, the conversion profiles are very similar. This is a characteristic of controlled process by NMRP. It can be seen in several studies in the literature<sup>8,21</sup> that NMRP process is not very sensitive to differences on temperature, differently from conventional process in which the reaction rate increase twice when elevating 10°C on bulk polymerization.

The PDI for the ratio equal to 3 : 1 and 4 : 1 at two different temperatures (125 and 135°C) can be found in Figure 4. This figure shows an unexpected result, confirmed for the four operating conditions considered. For all cases, the PDI is much higher



**Figure 4** PDI for temperatures 125 and 135°C and ratios 3 : 1 and 4 : 1. [Trigonox 301] = 0.0029 mol/L.



**Figure 5** Conversion profile. Initiator concentration of 0.0029 and 0.0058 mol/L.  $T = 130^{\circ}\text{C}$  and ratio [TEMPO]/[Initiator] = 4 : 1 for all the cases.

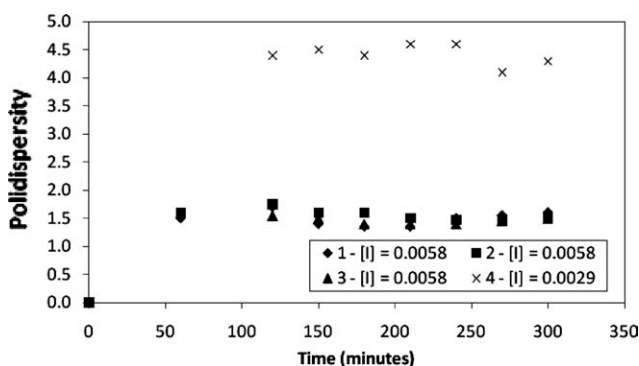
than the one expected for the case of controlled process (PDI lower than 1.5). In fact, the PDIs observed in Figure 4 are even bigger than the ones expected for the conventional polymerization of styrene.

This can be explained by the fact that maybe the PDI reached values greater than the ones for conventional process, because some chains grow freely, whereas others are captured by TEMPO. Consequently, polymers with a large discrepancy in terms of chain length are obtained.

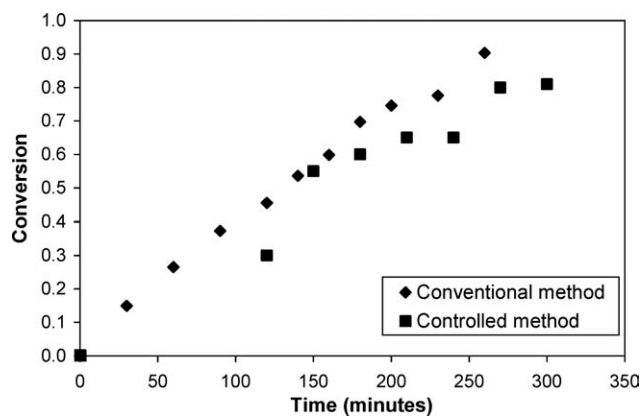
It was observed in some works of our group<sup>22</sup> that a simultaneous increase on initiator and controller concentration (keeping the ratio between them) generates polymers with lower PDI, so, as the next step, the polymerization was performed using initiator concentration equal to 0.0058 mol/L (twice the first attempt).

The conversion profiles for initiator concentration equal to 0.0029 and 0.0058 mol/L are shown in Figure 5. In this last case, the experiments were performed in triplicate (curves 1–3). It can be observed that when the concentration of initiator was multiplied by two, there was a significative increase on conversion, as expected.

The PDI profiles when concentrations of initiator equal to 0.0029 and 0.0058 mol/L were used can be found in Figure 6. For the last case, the PDI



**Figure 6** PDI profiles when using concentration of initiator equal to 0.0029 mol/L and after 0.0058 mol/L.  $T = 130^{\circ}\text{C}$  and ratio [TEMPO]/[Initiator] = 4 : 1 for all the cases.



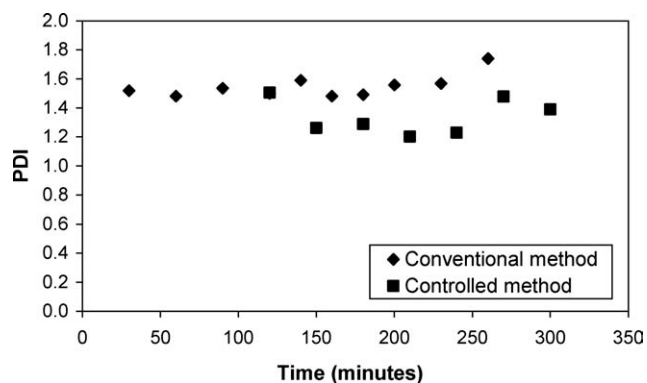
**Figure 7** Conversion profiles when using conventional and controlled polymerization. Temperature equal to 130°C, [Trigonox 301] = 0.0058 mol/L, and ratio [TEMPO]/[initiator] = 4 : 1 for NMRP.

measurements were done in triplicate (curves 1–3) to certify the results.

Analyzing Figure 6, it can be noted that there was a huge reduction on PDI when using twice the concentration of controller and initiator. In previous work from our group,<sup>23</sup> we concluded that in NMRP process, there is a secondary reaction between controller and initiator that must be considered in the NMRP mechanism. When using lower concentration of initiator (and consequently low concentration of controller, because the ratio is 4 : 1), maybe the consumption of controller by the secondary reaction between controller and initiator become important, promoting an imbalance between these two species, because there is a source of radicals from thermal initiation. Consequently, the polymerization becomes not controlled.

Following the same way, Figure 7 shows conversion profiles for the controlled and conventional polymerization. In both cases, initiator concentration is 0.0058 mol/L. The temperature is 130°C for both cases and the ratio [TEMPO]/[initiator] = 4 : 1 for the controlled polymerization. Figure 7 shows that, in terms of conversion, there is no significant difference between conventional and controlled methods. It is possible to notice a little increase on conversion to the conventional method. This fact indicates that the formation of the dormant alkoxyamine species decelerates the polymerization process, producing less polymer chains in the same interval of time.

Finally, Figure 8 shows the PDI profiles for controlled and conventional polymerization for the same operating condition used on Figure 6. It can be seen that the initiator Trigonox 301 is able to produce polymers with PDI lower than 2 for conventional polymerization, which is a low value when compared to the PDI obtained from other chemical initiator (monofunctional, bifunctional, or multifunc-



**Figure 8** PDI profiles when using conventional and controlled methods. Temperature equal to 130°C, [Trigonox 301] = 0.0058 mol/L, and ratio [TEMPO]/[initiator] = 4 : 1.

tional). On the other hand, the living radical polymerization using Trigonox 301 generates controlled polymer (PDI lower than 1.5), however the PDI values obtained are not as low as the ones obtained from other initiators, like benzoyl peroxide (BPO), for example, that is able to produce polymer with PDI very close to 1.0 in controlled polymerization.

For comparative reasons, Table I brings the average molecular weights obtained at the end of polymerization (conversion equal to 85%), in three different situations:

- Conventional polymerization using Trigonox 301 as initiator at concentration equal to 0.0058 mol/L;
- Controlled polymerization using Trigonox 301 as initiator at concentration equal to 0.0058 mol/L and ratio between controller and initiator equal to 4 : 1;
- Controlled polymerization using Trigonox 301 as initiator at concentration equal to 0.0029 mol/L and ratio between controller and initiator equal to 4 : 1.

In all cases, temperature equal to 130°C was considered:

In Table I, it is possible to see that  $\bar{M}_w$  is reduced one order of magnitude, when the initiator concentration is the double for the controlled polymerization. This happens maybe because when lower initiator concentration is used, many chains grow without any action of the controller (not controlled

**TABLE I**  
Comparison on Average Molecular Weights and PDI for Controlled and Conventional Polymerization Using Different Concentrations of Initiator

	Case a	Case b	Case c
$\bar{M}_w$	$1.247 \times 10^6$	$1.479 \times 10^4$	$1.126 \times 10^5$
PDI	1.70	1.50	4.21



process), reaching very long length. It can also be observed that the molecular weight for the conventional polymerization is very high (around  $10^6$ ), when Trigonox 301 is used, and the PDI is lower than two. It can be observed that the controlled process can reduce the PDI, however, the  $\overline{M}_w$  is also reduced in almost two orders of magnitude.

### CONCLUSIONS

In this work, the use of the cyclic trifunctional initiator (Trigonox 301) on controlled (NMRP) and conventional polymerization was investigated.

It was observed that the conventional polymerization is able to produce polymers with very high average molecular weight (around  $10^6$ ) and PDIs lower than 2.0.

When using controlled polymerization (NMRP), it is possible to reduce the PDI (lower than 1.5), however, the average molecular weight decreases around two orders of magnitude (around  $10^4$ ) when compared to the conventional process.

For the controlled process, the operating conditions used have a huge effect on the properties of the polymer. If lower concentration of initiator and controller is used, for example, PDI around 4 can be obtained, which is much higher than those obtained with the conventional polymerization. This might happen, because some chains are kept trapped, whereas others freely increase, generating a large MWD.

In conclusion, multifunctional initiator should be used carefully in NMRP process.

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