

Cyclic Trifunctional Peroxide On Living Free Radical Polymerization

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Until the mid 90's, free radical polymerization (FRP) was characterized by producing polymers with high average molecular weights (1×10^5 - 1×10^6) since the beginning of polymerization, index of polydispersity (PDI) greater than 1.5 and wide molecular weight distribution (MWD). When necessary to produce polymers with more defined structure, it was usually used anionic polymerization, which is capable to produce polymers with narrow molecular weight distribution and PDI around 1.0 (1.1-1.2). The ionic polymerization, however, needs to be held in a high degree of purity and in the absence of inhibitors, what make the ionic polymerization expensive and not very practical from the industrial point of view. A promising alternative to ionic polymerization has been the living radical polymerization (LFRP), which is much more robust to the impurities and kind of solvent and it is able to produce polymers with polydispersity close to one. Nevertheless, the LFRP presents lower polymerization rates compared to standard and smaller polymer chains (lower molecular weights averages). In this work the effect of cyclic trifunctional initiator on the Living Free Radical Polymerization is analyzed. The Nitroxide Mediated Radical Polymerization (NMRP) is considered, using TEMPO as controller and styrene as monomer. It can be observed that the polydispersity can vary in a very broad range when this initiator is used, changing from PDI lower than 1.5 until PDI bigger than 4.0, depending on the operating conditions considered.

1. Introduction

In this work it was performed the polymerization of styrene on living free radical mediated by nitroxide. As initiator it was used the Trigonox 301 (3,6,9-Triethyl-3,6,9-trimethyl-1,4,7-triperoxonane), kindly supplied by Akzo Nobel company. This is a cyclic trifunctional initiator, able to generate a larger quantity of radicals if compared with mono and bifunctional initiator. The three bonds oxygen – oxygen that can to break easily, releasing, therefore, six free radicals by molecule. The TEMPO was the controller used.

Our group has studied different kind of initiators on NMRP process in order to accelerate the polymerization rate. Monofunctional initiator with low decomposition rate, like TBEC was used in substitution to more conventional ones, like BPO and AIBN (Dias et al. 2007). We observed that TBEC is able to accelerate twice the reaction rate keeping the polydispersity of the polymer close to 1.0.

In other study, we used difunctional initiator on NMRP process and showed that it is possible to accelerate the polymerization rate and increase the molecular weight of the polymer keeping the controlled microstructure of the produced polymer (PDI close to the unity).

Our group also studied the cyclic trifunctional initiator TRIGONOX 301 on standard free radical polymerization. In standard polymerization, the molecular weights obtained are very high (close to 10^6 daltons), when compared to the ones obtained from mono and difunctional initiator. In this work the performance of the cyclic trifunctional peroxide is verified on the NMRP process.

2. Experimental

The experimental conditions studied were four: time of reaction, temperature, ration controller/initiator and concentration of initiator.

To accompany the results, four parameters were valued, namely: conversion, polydispersity, average molecular weight (M_n) and average numeric molecular weight (M_w). These were obtained by GPC (Gel Permeation Chromatograph).

The monomer is purified from any inhibitor added by the manufacturer (to ensure safe transport and storage). The styrene is washed three times with a 10w/v % sodium hydroxide solution and then three times with deionized water. After washing, the monomer is placed in a flask with pelleted calcium chloride, which acts as agent drying. The next step is the distillation of monomer, which is made in vertical rotary evaporator, equipped with a vacuum pump and heated bath.

Quantities of desired monomer (styrene), initiator (Trigonox 301) and controller (TEMPO) are heavy in analytical balance and added in a bottle. Add a quantity of the solution monomer-initiator-controller in ampoules, which are connected into a panel support, in order to keep them inside a container with liquid nitrogen and allow exhaust system using a vacuum pump. After freezing of the solution, binds the vacuum for the removal of oxygen, which acts as inhibitor. Each ampoule is then sealed using a torch with fire. The ampoules are placed in a bath of oil heated with circulation of the fluid to a certain temperature, which occur the reactions of polymerization. The ampoules are withdrawn at various intervals of time pre-set, and placed in baths of ice and then liquid nitrogen to stop the reaction. After weighing, the mixture is removed from ampoules and conversion can be calculated gravimetrically. The mixture polymer/monomer is dissolved using methylene chloride and then precipitated with ethanol or methanol. After evaporation of all solvent inside the chapel with forced movement, dries up the samples in a vacuum dryer for total removal of monomer and solvent. The polymer is characterized by a GEL Permeation Chromatography (GPC) with triple detector (viscometer, light scattering (RALLS) and refractive index (RI)). It was also done Rays-X Diffractometry (RXD)'s analyses to investigate the physical morphology of the

polymer. Straightforwardly by explanation's questions, it will be showed soon below chemical structures of the initiator and controller.

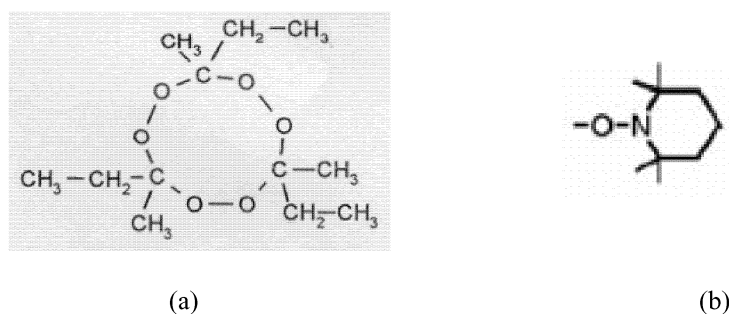


Figure 1: Chemical structure of the initiator (a) and controller (b).

3. Results and discussions

The experimental runs were performed at three different temperatures (125, 130 and 135°C). In the same way, three ratios [controller]/[initiator] also were performed (3:1, 4:1 and 5:1) in every one of the temperatures. Those ones with ratio equal to 5:1 resulted in a conversion very low and, therefore, its samples were not analyzed in GPC. For all case the initiator concentration used was 0,0029 mol/l. The 2 below shows these results. The 2a and 2b show that temperature does not have a significant effect on the conversion profiles. The ratio [controller]/[initiator] is an important parameter to be considered. When ratio is equal to 5:1, less than 10% of conversion was obtained after 300 minutes of reaction, very different from the results obtained hen ratio 3:1 and 4:1 is used (around 60% of conversion at 300 minutes).

Figures 2c and 2d show that for all operating conditions used, very high polydispersity is obtained (close to 4). This is a very interesting characteristic, because the polydispersity obtained on controlled process is much higher than the one obtained in standard polymerization using this some cyclic initiators (PDI about 1.8 for standard polymerization - not shown).

On the other hand, one can not say that controlled polymer could be obtained at the studied operating condition with TRIGONOX 301.

The values of molecular weights obtained are reasonable (around 10^5 daltons) and there is no significant effect of temperature and ratio [controller]/[initiator] on the molecular weights average (see figures 2e, 2f, 2g and 2h).

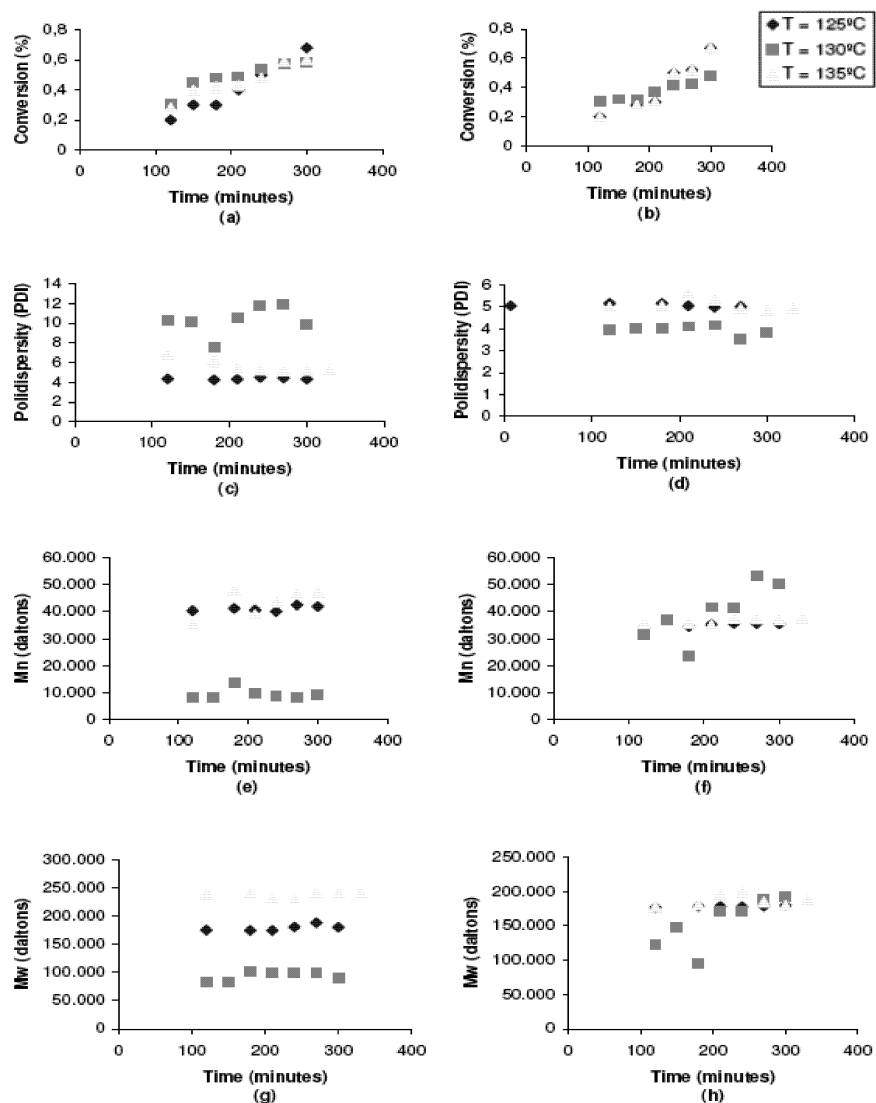


Figure 2: (a) Conversion to the ratio equal to 3:1; (b) Conversion to the ratio equal to 4:1; (c) Polidispersity to the ratio equal to 3:1; (d) Polidispersity to the ratio equal to 4:1; (e) Mn to the ratio equal to 3:1; (f) Mn to the ratio equal to 4:1; (g) Mw to the ratio equal to 3:1; (h) Mw to the ratio equal to 4:1.

The next variable to be changed in order to try lower polidispersity was the concentration of initiator, kept on 0,0029 mol/L for all previous experiments. The figure 3 shows results obtained when initiator concentration was 0,0058 mol/L. For this condition, the temperature used was 130°C and the ratio [controller]/[initiator] was 4:1. The experiments were performed in triplicate, as can be seen on figure 3.

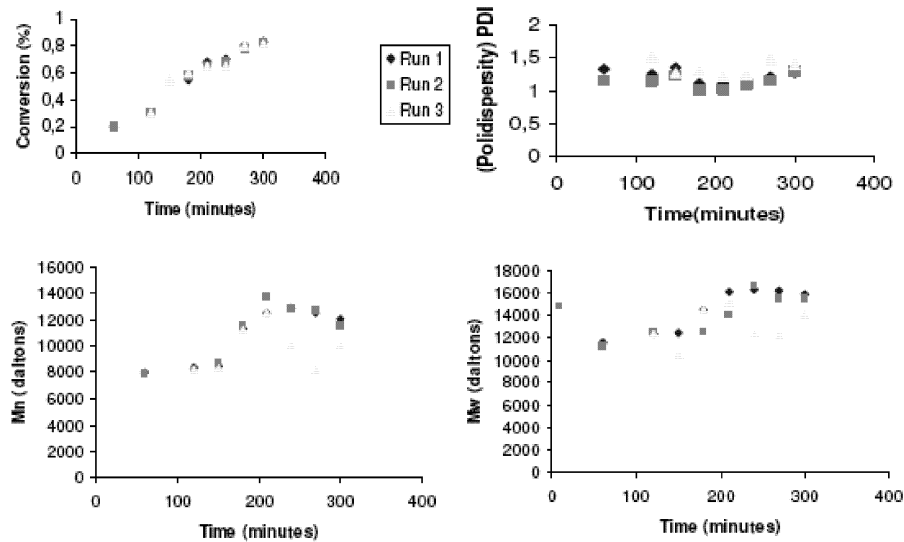


Figure 3: Conversion, PDI and molecular weight profiles when $[I] = 0,0058 \text{ mol/L}$. Ratio between $[\text{controller}]/[\text{initiator}]$ equal to 4:1 and temperature equal to 130°C .

As we can see in figure 3, at this condition the control of the process took place. This means that it is necessary and indispensable a correct relationship among temperature, ratio $[\text{controller}]/[\text{initiator}]$ and concentration of initiator for to achieve the desirable process. According to Cerna et al. (2002) there are two different mechanism for the initiator's decomposition: thermal and not thermal (see figure 4). In the first of them, all the initiator's decomposition is started in beginning of the process and, consequently, occurs a faster liberation of free radicals, which provoke the instantaneous growth of the chains. Maybe because this mechanism of the TEMPO is not quick enough to establish a good equilibrium between dormant and active chains when low concentration of initiator and controller are used. Besides, a RXD analyses was performed for the polymer that shows low PDI (figure 5).

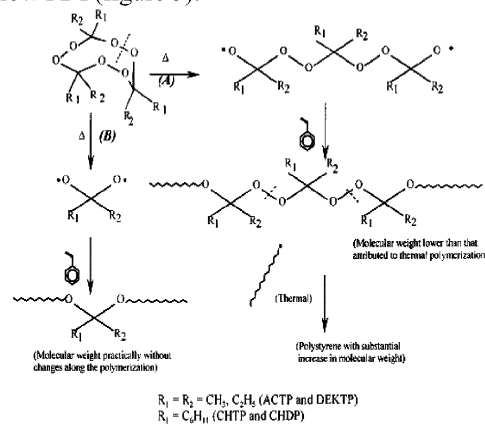


Figure 4: Different ways to the initiator's decomposition.

The figure below shows the obtained result by Rays-X Diffratometry.

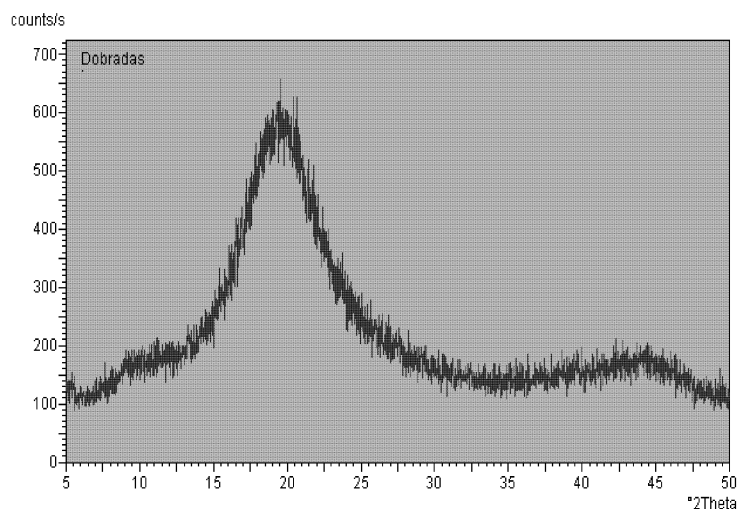


Figure 5: Rays-X Diffratometry's result.

By the figure 4 it is possible to perceive that the peak obtained is referent to the amorphous polystyrene, which is very few crystalline.

4. Conclusions

In this work nitroxide mediated polymerization was performed using the cyclic trifunctional peroxide – TRIGONOX 301. It was observed that controlled process only will be reached when a satisfactory relationship among the key parameters: concentration of initiator, ratio [controller]/[initiator] and temperature is established.

5. References

- Cerna, J.R.; Morales, G.; Eyler, G.N.; Canizo, A.I. (2002), "Bulk Polymerization of Styrene Catalyzed by Bi- and Trifunctional Cyclic Initiators", *J. Applied Polymer Sci.*, Vol. 83, pp. 1-11.
- Dias, R. S.; Gonçalves, M. C., Lona, L. M. F., Vivaldo-Lima, E., McManus, N. T., Penlidis, A; "Nitroxide – Mediated Radical Polymerization of Styrene Using Mono and Di – Functional Initiators", *Chemical Engineering Science*, 16 December 2006.