

EXPERIMENTAL STUDY OF LIVING FREE RADICAL POLYMERIZATION USING TRIFUNCTIONAL INITIATOR AND POLYMERIZATION MEDIATED BY NITROXIDES

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ABSTRACT

Controlled free radical polymerization or Living Free Radical Polymerization (LFRP) has received increasing attention as a technique for the production of polymers with microstructure highly controlled. In particular, narrow molecular weight distributions are obtained with polydispersity very close to one. In this research it was investigate the controlled polymerization mediated by nitroxides, using a cyclic trifunctional peroxide. As long as we know, there are only publications in literature dealing with NMRP using mono- and bi-functional initiators. It was believed that the trifunctional peroxide can increase the rate of polymerization, since more free radicals are generated, if compared with initiators with lower functionality. Furthermore, the fact of the initiator be cyclic means that branches are not generated in the chains, which theoretically prevents an increase in polydispersity of the polymer. The effect of the dissociation constant of the trifunctional initiator in the velocity of the reaction was analyzed.

Keywords: *radicalar polymerization; controlled polymerization; multifunctional initiator*

Introduction

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 (MWD) distribution. 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. An important alternative to escape this problem is the Controlled Free Radical Polymerization. This, in your turn, is much more robust to impurities and kind of solvent and it is able to produce polymers with polydispersity close to one.

One of the routes for Controlled Free Radical Polymerization is the Nitroxide Mediated Radical Polymerization (NMRP) that uses a stable nitroxide radical to capture the chains in growth.

The NMRP utilizes frequently the TEMPO (2,2,6,6, tetrametil-1-piperidinoxil) like controller agent. His actuation's mechanism can be showed by following equation:



where:

R – X: dormant polymeric chains (deactivated).

R•: radical polymeric in growth (activated).

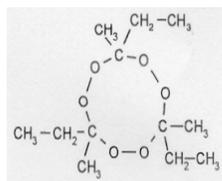
X•: capturing agents

ka: kinetic constant of the activation's rate of the reaction of activation – deactivation.

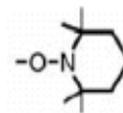
kda: kinetic constant of the deactivation's rate of the reaction of activation – deactivation.

Due to the reversible reaction, the polymerization rate becomes slower when compared to the Standard Free Radical Polymerization. Our group has tried contoured this problem using bifunctional initiators, which are able to increase a velocity of reaction maintaining the characteristics of the polymer.

In this work it was performed the controlled polymerization of styrene using as initiator the Trigonox 301 (3,6,9-Triethyl-3,6,9-trimethyl-1,4,7-triperoxoname), kindly supplied by Akzo Nobel company. The Trigonox 301 is a very instable initiator because it presents a cyclic chemical structure with three oxygen – oxygen bonds. The TEMPO was the controller used. The chemical structure of initiator and controller can be seen on Figure 1.



Trigonox 301



TEMPO

Figure 1: Chemical Structures of the initiator and controller.

The experimental conditions studied took into account 2 different levels of temperature, ratio between controller/initiator and concentration of initiator. Four parameters were analyzed: conversion, polydispersity, number average molecular weight (M_n) and weight average numeric molecular weight (M_w).

The molecular weights were obtained by GPC (Gel Permeation Chromatograph) and the final chemical structure of the synthesized polymer was obtained using Diffractometry of X-Ray (DRX) and Nuclear Magnetic Resonance of protons (NMR).

Experimental

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.

Desired quantities of monomer (styrene), initiator (Trigonox 301) and controller (TEMPO) were weighed, mixed and added into ampoules. It is used three cycles of freeze/ thaw under vacuum in order to remove the oxygen from the ampoules. After torch-sealing, the ampoules were placed into an oil bath at a given temperature. Ampoules were withdrawn at pre-set times, and the reaction

was stopped with an ice bath and then with liquid nitrogen. The ampoules were weighed, broken and the polymer/monomer mixture was dissolved in methylene chloride, and precipitated with ethanol. After evaporation of solvent and monomer, monomer conversion was obtained gravimetrically. The polymer product was characterized by Gel Permeation Chromatograph that was based on a detector system with low and high angle laser light scattering, viscometer and refractive index (RI).

Results and discussions

The experimental runs were performed at two temperature different (125 and 135°C). In the same way, three ratios [controller]/[initiator] were also performed (3:1, 4:1 and 5:1) in every one of the temperatures. When ratio equal to 5:1 was considered, very low conversion was obtained (lower than 10%), and therefore, the samples were not analyzed in GPC. The figure 2 shows conversion, polydispersity and molecular weight profiles. In all the cases two temperatures were considered (125 and 135°C) and the initiator concentration used was 0.0029 mol/L.

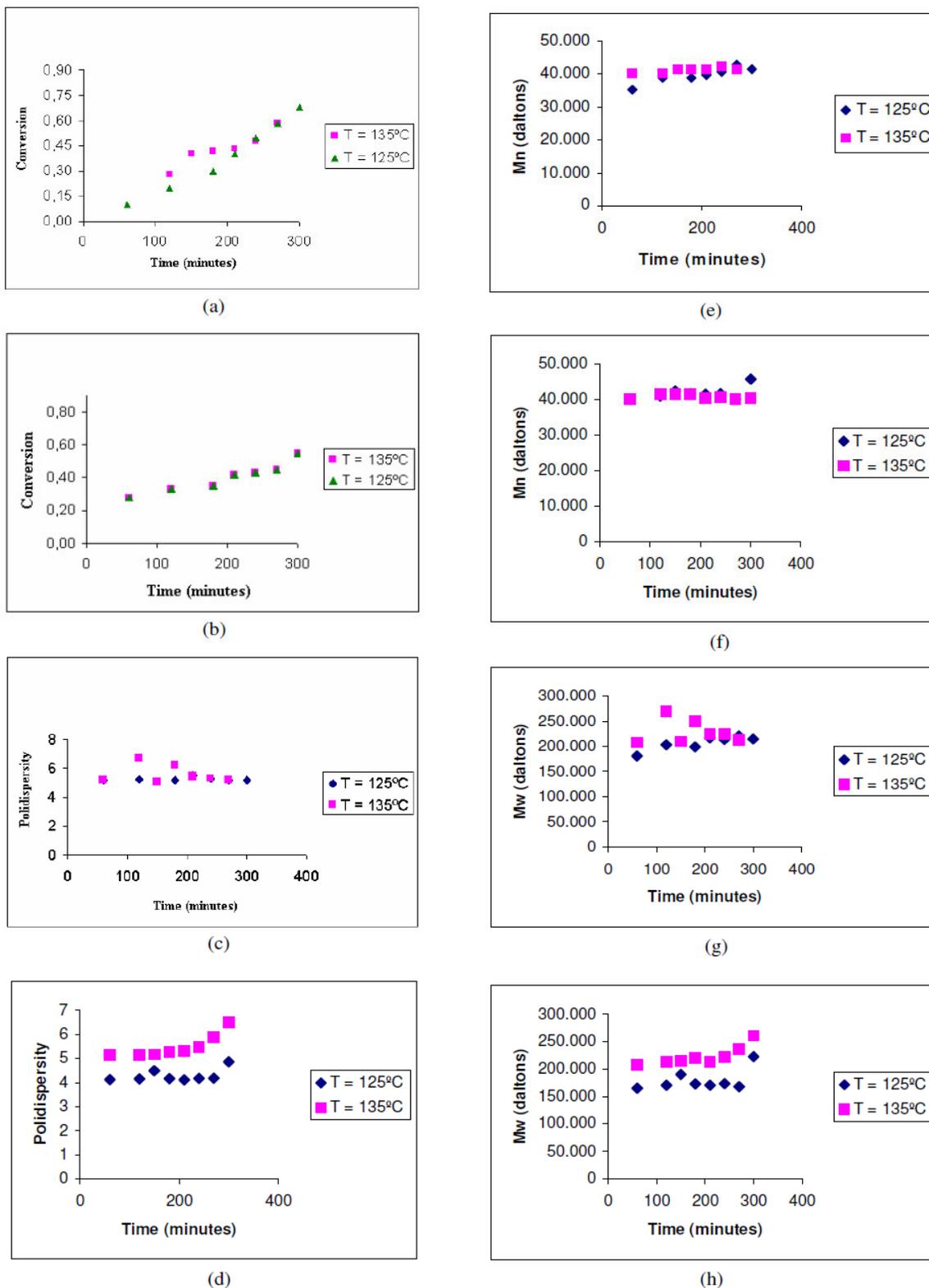


Figure 2: (a) Conversion to the ratio equal to 3:1; (b) Conversion to the ratio equal to 4:1; (c) Polidispersity to the ratio equal to 3:1; (d) Polidispersity to the ratio equal to 4:1; (e) Mn to the ratio equal to 3:1; (f) Mn to the ratio equal to 4:1; (g) Mw to the ratio equal to 3:1; (h) Mw to the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

It can be observed that in all cases it was not possible to obtain controlled polymer, because the polydispersity is much bigger than the unity. Maybe this occurs because a low concentration of initiator is being used. It is known that the controller can react with the initiator to produce inert compounds. If this is the case, the concentration of controller can not be enough to capture all growing chains, generating some dormant chains and some chains that never get trapped. This could generate an ever higher polydispersity if compared to the standard polymerization.

As a second alternative the concentration of the initiator was increased to 0.0058 mol/L, keeping the previous rates used before. Figure 3 shows conversion, polydispersity and molecular weights obtained when higher concentration of initiator is used. The experiments were performed in triplicates and in all the cases it can be seen a controlled polymer being produced, with polydispersity close to one.

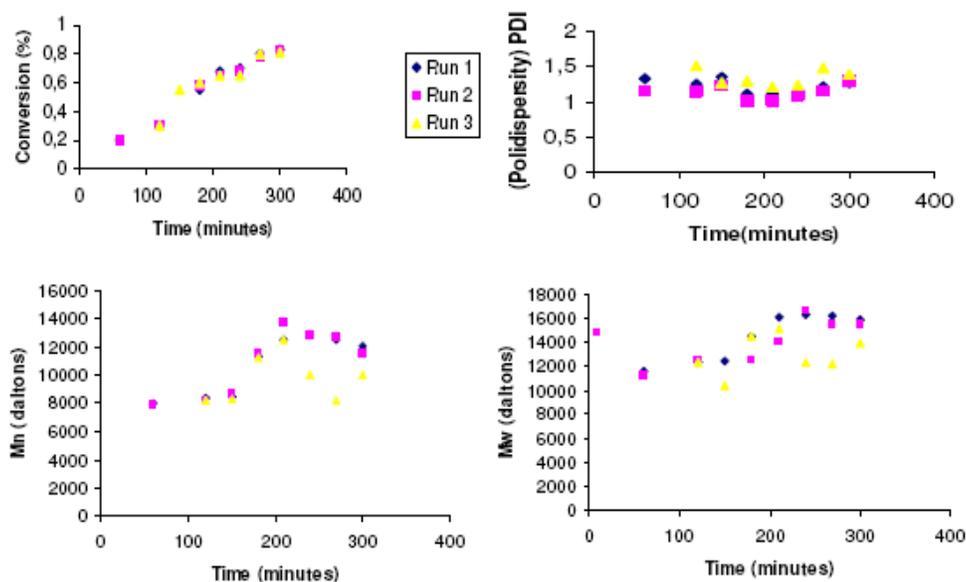


Figure 3: Obtained results to the rehearsal with the initial concentration of initiator multiplied by two. Ratio between [controller]/[initiator] equal to 4:1 and temperature equal to 130°C.

This means that it is necessary and indispensable a correct relationship among temperature, ratio [controller]/[initiator] and concentration of initiator to achieve the desirable process. Even it being a controlled process the time of reaction was not significantly changed.

Cerna et al (2002) explain that there are two different ways for the decomposition of the Trigonox 301: thermal and not thermal, as can be seen in Figure 4. In first one, the decomposition of all initiator starts in beginning of the process and, consequently, occurs a faster liberation of free radicals, which provoke the instantaneous growth of the chains. This way, the action's mechanism

of the TEMPO is not quick enough to establish a good equilibrium of the chemical reaction showed in equation 1. The result consists in a disordered polymer production with high polydispersity.

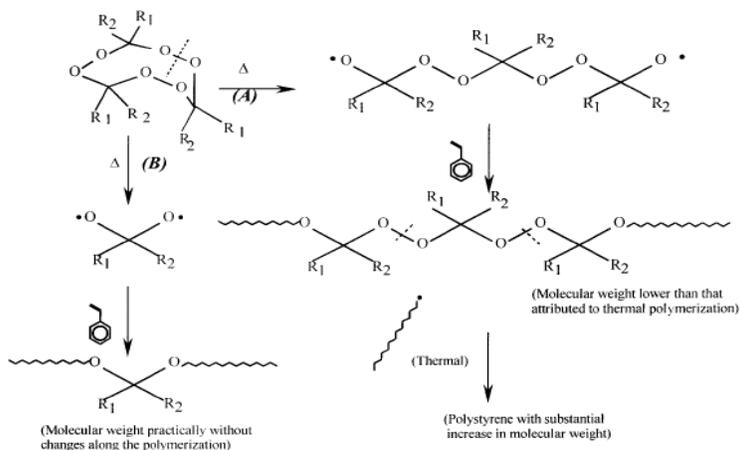


Figure 4: Different ways to the initiator's decomposition (Cerna et al., 2002).

For the sample of the controlled polymer it was done analyses of RMN e DRX. These results are shown in Figure 5:

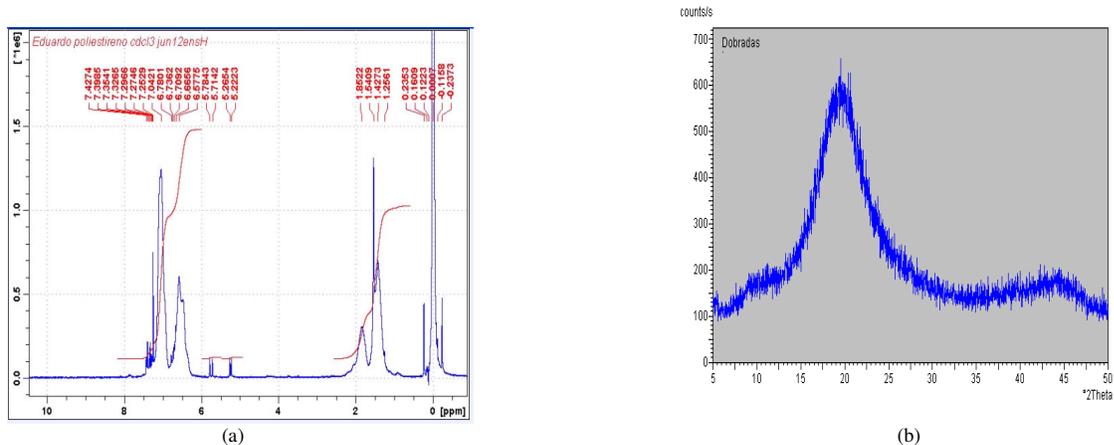


Figure 5: RMN (a) and DRX (b) results.

Taking a look in the figure 5, we can observe that the RMN spectrum give us the polystyrene's synthesis confirmation, because the peak referent to the displacement of 7,0421 ppm correspond to the four atoms of hydrogen fixed in aromatic ring. This is a crucial characteristic to determinate the real presence of this compound in sample. Nevertheless, the peaks of lower intensity have showed to us that there is still monomer remaining in reaction environment. With regard to the DRX results, it can be said that the shape of the peak obtained corresponds, doubtless, to a polymer with random chemical structure, in other words, the final product is amorphous.

Conclusions

A controlled process only will be reached when it is observed a satisfactory relationship among the key parameters: concentration of initiator, ratio [controller]/[initiator] and temperature. Just with a higher concentration of initiator we could obtain controlled polymer. The technique of controlled free radical polymerization is versatile and produces polymers with narrower molecular weight distributions and lower polydispersity.

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