

TEMPO-MEDIATED FREE RADICAL COPOLYMERIZATION OF STYRENE AND DIVINYLBENZENE

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Nitroxide-mediated radical copolymerization (NMRP) of styrene and small amounts of divinylbenzene, using 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO) as controller and tert-butylperoxy-2-ethylhexyl carbonate (TBEC) as initiator, was performed with the purpose of enhancing the reaction rate while keeping the controlled and living characteristics of the polymer synthesized (low polydispersity and molecular weights increasing linearly with conversion). It was shown that at certain operating conditions it is possible to enhance the polymerization rate and produce polymers with polydispersity close to the unity.

Keywords: *Controlled, copolymerization, styrene, divinylbenzene.*

Introduction

Living or pseudo-living free radical polymerization is a promising route for the production of polymers with highly controlled microstructure (narrow molecular weights distributions). Living free radical polymerization is different from the standard free radical polymerization route due to a reversible reaction that makes the chains experience frequent cycles of radical activation-deactivation over the period of polymerization. As a result all the chains have an approximately equal chance of growing, which leads to a low polydispersity of the final product. Free radical polymerization pathways, are more versatile in relation to viable monomers and are more robust to impurities than traditional ionic (anionic and cationic) polymerization methods, and so offer an attractive alternative production route to polymers with controlled structures.

One disadvantage of controlled polymerization process is related to the low polymerization rate, due to the reversible reaction that maintains the polymer chain as a dormant species for long periods of time. In the literature, most of the papers on NMRP use BPO or AIBN as initiator (Butté et al., 1999, Bonilla et al., 2002, Tuinman et al., 2006). The objective of this work is to try to enhance the polymerization rate by using a different kind of initiator (tert-butylperoxy-2-ethylhexyl carbonate - TBEC), that has a lower decomposition rate, compared to BPO and AIBN.

There are some published works on living polymerization. Santos et al. (2009) studied RAFT polymerization of styrene in aqueous dispersed system and had polymers with a broad molar mass distribution. Lenzi et al. (2005) produced polystyrene with bimodal molecular weight distribution by the sequential use of nitroxide mediated and conventional free radical techniques. Asteasuain et al. (2007) developed a mathematical model of the nitroxide mediated living free radical polymerization of styrene in a tubular reactor.

Most of the published works on NMRP address the homopolymerization of styrene. Tuinman et al. (2006) performed the co-polymerization of styrene-divinylbenzene (Sty-DVB), but using BPO as initiator. In this work, we investigated, the copolymerization of

styrene and divinylbenzene by living polymerization (NMRP), using TEMPO as controller, and TBEC as the initiator. Divinylbenzene acts as a branching generator and has a high probability of generating crosslinks, giving more resistance to the polymer.

All the experiments were performed in sealed ampoules. To better understand this system, a set of designed experiments were performed at different temperatures, DVB concentrations, initiator concentrations and molar ratios between controller and initiator.

Experimental

TEMPO (Acros Organics, 98%), tert-butylperoxy-2-ethylhexyl carbonate (TBEC) (Sigma-Aldrich, 95%) and divinylbenzene (Sigma-Aldrich, 80%) were used as received.

In order to purify styrene (Sigma-Aldrich, 99%) it was washed for three times with an aqueous NaOH solution and then deionized water. After that it was dried over calcium chloride and distilled under vacuum. Desired quantities of styrene, divinylbenzene, initiator and controller were weighed, mixed and then placed in ampoules. These ampoules were degassed by three freeze/ thaw cycles under vacuum in order to remove the oxygen. After sealing the ampoules were placed in a temperature controlled oil bath at a selected temperature. Ampoules were withdrawn at pre-set time intervals. The ampoules were weighed, broken and the polymer/monomer mixture was dissolved in methylene chloride, and precipitated with ethanol. After the evaporation of solvent and monomer the conversion was obtained by gravimetric method. The polymer 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 Discussion

Table 1 shows a comparison between the TBEC and BPO performance on the copolymerization of styrene and divinylbenzene considering initiator concentration equal to 0.036 mol/l, molar ratio between TEMPO and initiator equal to 1.4 and mass fraction of divinylbenzene equal to 1%. For all cases it was analyzed the time needed to reach conversion equal to 40%. It can be seen a significant reduction of polymerization time when TBEC is used.

Table 1: Time needed for reach conversion of 40% considering TBEC and BPO initiators.

	TEMPERATURE (°C)	TIME (MIN)
BPO*	120	600
BPO*	130	342
TBEC	125	108
TBEC	135	50

*Experimental results obtained from our group

Figure 1 shows the effect of initiator type on the number average molecular weight. This type of polymerization leads to crosslinked polymer which after reaching a critical level of crosslinking produces fractions of insoluble material. The values of molecular weight obtained are only for the soluble fraction of the polymer obtained. It can be observed that in both runs (TBEC and BPO) the number average molecular weights increase linearly with the conversion which is a characteristic of controlled process. Also, similar values of molecular weight were obtained for both initiators.

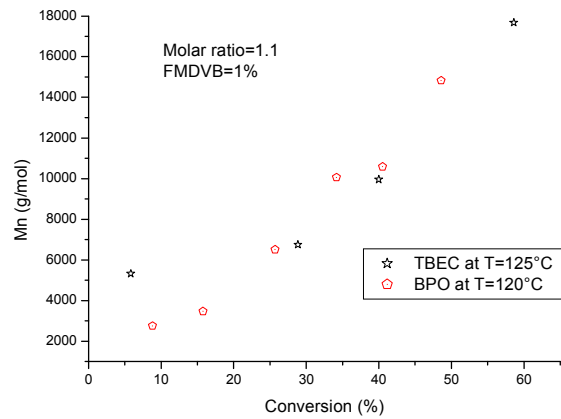


Figure 1: Effect of the initiator type on the number average molecular weight, for the NMRP process.

After comparing the performance of both initiators, polymerizations using TBEC were performed at different operating conditions (two levels of temperature, initiator concentration, weight fraction of DVB and TEMPO/TBEC molar ratio, as show in table 2).

Table 2: Summary of the experimental conditions for NMRP process of styrene/ DVB copolymerization using TBEC as initiator

RUNS	TEMPERATURE (°C)	INITIATOR CONCENTRATION (M)	MOLAR RATIO (R=[TEMPO]/[I])	WEIGHT FRACTION DVB (%)
1	125	0.0029	1.1	1
2	135	0.0029	1.1	1
3	125	0.036	1.1	1
4	135	0.036	1.1	1
5	125	0.0029	1.4	1
6	135	0.0029	1.4	1
7	125	0.036	1.4	1
8	135	0.036	1.4	1
9	125	0.0029	1.1	1.5
10	135	0.0029	1.1	1.5
11	125	0.036	1.1	1.5
12	135	0.036	1.1	1.5
13	125	0.0029	1.4	1.5
14	135	0.0029	1.4	1.5
15	125	0.036	1.4	1.5
16	135	0.036	1.4	1.5
17	130	0.0195	1.25	1.25
18	130	0.0195	1.25	1.25
19	130	0.0195	1.25	1.25

In figures 2 and 3 the effect of a simultaneous increase in TEMPO and initiator concentrations (with molar ratio (1.1) between them) for the temperature of 125°C and

mass fraction of DVB equal to 1% is shown in relation to conversion and polydispersity, respectively. It can be noticed, by figure 2 that, as expected, there was a significant increase in the conversion versus time profiles for the experiments that used larger initiator and controller concentrations. This condition favors a pronounced increase on radical concentrations, consequently increasing the reaction rate. Through the figure 3, it can be observed that higher values of polydispersity are obtained at lower concentrations of the initiator. It can be noticed that after the gelation point for the run with TBEC concentration equal to 0.0029 mol/l there is a drop on polydispersity because only the soluble fraction is analyzed.

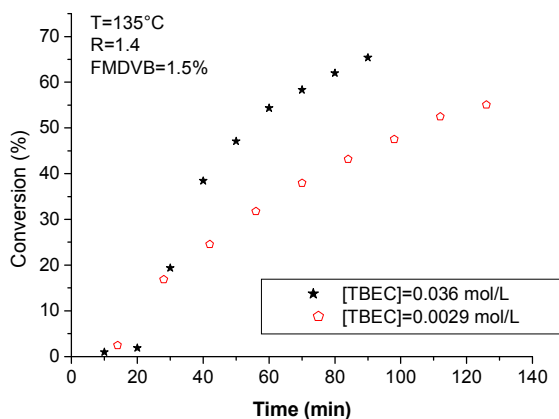


Figure 2: Effect of the increase on the TBEC and TEMPO concentration on the rate of polymerization, for the NMRP process

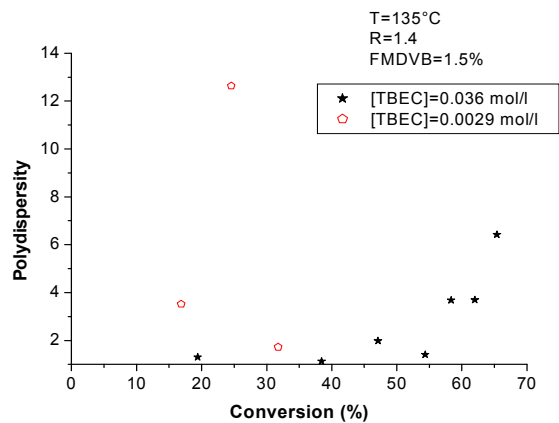


Figure 3: Effect of the increase on the TBEC and TEMPO concentration on polydispersity, for the NMRP process

Figures 4 to 5 show the effect of the temperature on the rate of polymerization and polydispersity, respectively. As expected, it can be noticed that an increase of 10°C on the temperature caused acceleration on the conversion profile.

It can be noticed that the polydispersity is very close for both temperature, which shows that the temperature apparently has low influence on the polymer properties for controlled polymerization. Similar results were described by Dias et al (2007) and Ximenes et al. (2007) for controlled homopolymerization of styrene.

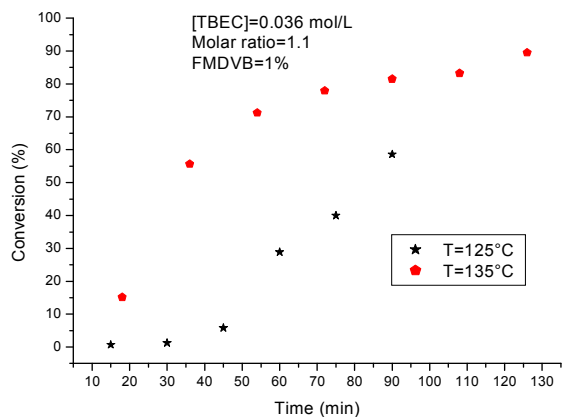


Figure 4: Effect of the temperature on the rate of polymerization, for the NMRP process

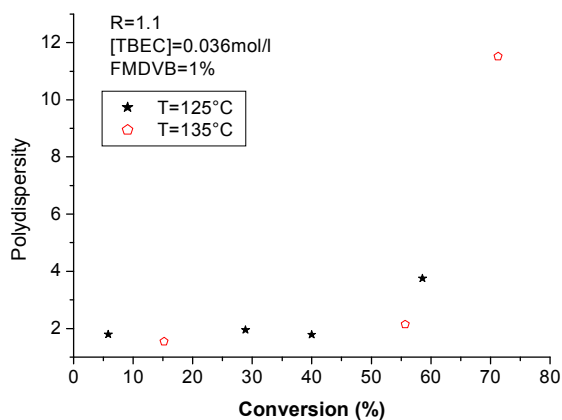


Figure 5: Effect of the temperature on the polydispersity, for the NMRP process

Figures 6 to 7 show the effect of the molar ratio of TEMPO and TBEC on the rate of polymerization and polydispersity, respectively. It can be observed that an increase in the TEMPO concentration maintaining the same initiator concentration caused a decrease in the rate of polymerization, as expected. This happens because a higher concentration of TEMPO affects the equilibrium leading to higher concentrations of dormant chains.

By the figure 6 it can be noticed that there is an increase on the induction period when a larger molar ratio between TEMPO and TBEC is used. It occurs because a larger concentration of nitroxide radicals will take a longer time to be consumed by the initiator forming dormant molecules.

It can be seen on figure 7 that the effect of the molar ratio between TEMPO and TBEC have low influence on polydispersity.

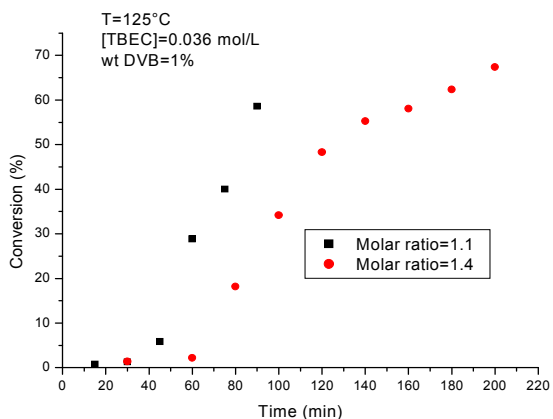


Figure 6: Effect of the molar ratio of [TEMPO] to [TBEC] on the rate of polymerization

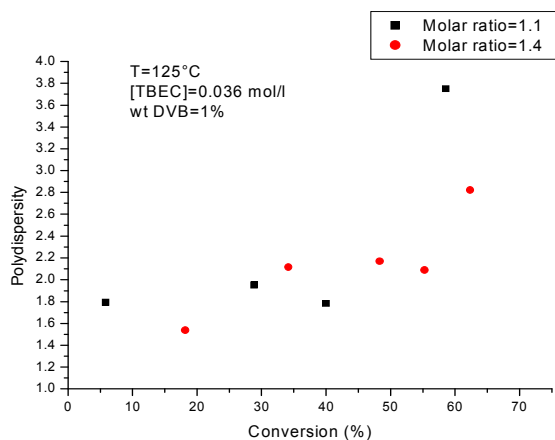


Figure 7: Effect of the molar ratio of [TEMPO] to [TBEC] on the polydispersity

Figures 8 show the effect of the weight fraction of divinylbenzene on the rate of polymerization. This result shows that the weight fraction of the DVB has low influence on the rate of polymerization as it was reported in the Tuinman et al. (2006) for BPO initiator.

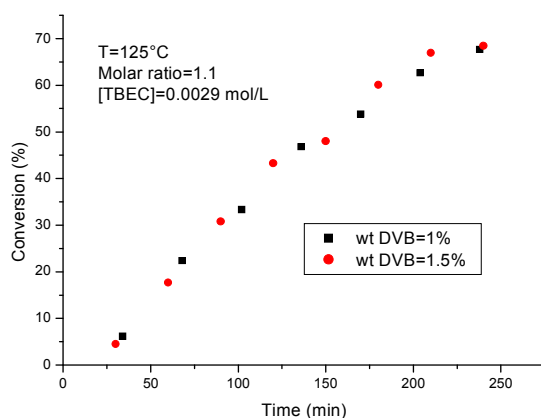


Figure 8: Effect of the weight fraction of DVB on the rate of polymerization

Conclusions

It was observed that TBEC initiator was able to considerably increase the velocity the reaction rate, preserving similar properties of the polymer (molecular weights and polydispersity) when compared to the case with BPO.

Through results analysis it can be noticed that the parameters that most influenced the rate of polymerization were the temperature, molar ratio between TEMPO to TBEC and controller and initiator concentration. The parameters that most influenced in polydispersity values were the molar ratio between controller and initiator and the initiator and controller concentration.

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