J Mater Sci (2010) 45:1878–1884
DOI 10.1007/s10853-009-4172-6

Nitroxide-mediated radical copolymerization of styrene and divinylbenzene: increased polymerization rate by using TBEC as initiator

T. R. Nogueira · L. M. F. Lona · N. T. McManus · E. Vivaldo-Lima · A. Penlidis

Received: 15 September 2009 / Accepted: 28 December 2009 / Published online: 12 January 2010

Abstract Nitroxide-mediated radical copolymerizations of styrene and divinylbenzene using 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO) as controller were performed to produce crosslinked polymers. *Tert*-butylperoxy 2-ethylhexyl carbonate (TBEC) was used instead of conventional initiators such as benzoyl peroxide (BPO) in order to enhance the polymerization rate while trying to keep the controlled characteristics of the system. The effect of temperature, initial concentration of initiator, and ratio of TEMPO to initiator on conversion, molecular weight averages, and polydispersity was investigated. It was observed that, when using TBEC, it was possible to produce controlled copolymer in a faster rate when compared to conventional initiators, like BPO.

Introduction

Controlled (living) free radical polymerization is a promising route for the production of polymers with highly controlled microstructure. Many groups have studied the kinetics of living free radical polymerization, but most of them considered the homopolymerization with standard initiators like benzoyl peroxide (BPO) [1–3] and 2,2′-azo-bis-iso-butyronitrile (AIBN) [4–6]. Dias et al. [7] showed that *tert*-butylperoxy 2-ethylhexyl carbonate (TBEC) initiator was able to increase considerably the reaction rate of controlled homopolymerization of styrene, while keeping the living characteristics of the system. Similar findings had been reported earlier by Goto and Fukuda [8] and Greszta and Matyjaszewski [9] for the monomolecular process.

Few studies have dealt with the controlled radical copolymerization of styrene and divinylbenzene (DVB). DVB acts as a branching generator, improving the polystyrene properties of resistance to impact and solvent. According to Ide and Fukuda [10], the gel generated in a controlled process is much more homogeneous and presents less intrachain cross-links. Tsoukatos et al. [11] and Tuinman et al. [3] studied the controlled copolymerization of styrene and DVB, using BPO as initiator. Slow reactions were observed (the time to reach conversions close to 50% varied from hours to days in these articles). In Tuinman et al. [3], the polymerization of styrene and DVB was investigated with a bimolecular initiation process using BPO as initiator and 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO) as controller. It was shown that the addition of DVB did not change considerably the polymerization rate and the polymerizations were quite slow. By analysis of the molecular weight profiles, it was shown that the molecular weight averages increased linearly with conversion until just before the gelation point, when there was an abrupt increase in weight average molecular weights, a situation typical for crosslinking polymerization systems.

As a continuation of the Tuinman et al. [3] study, the objective of the present work was to enhance the polymerization rate of controlled copolymerization of styrene–

T. R. Nogueira · L. M. F. Lona (✉)
Chemical Engineering School, University of Campinas,
Campinas, SP, Brazil
e-mail: liliane@feq.unicamp.br

T. R. Nogueira
e-mail: telma.nogueira@gmail.com

N. T. McManus · A. Penlidis
Institute for Polymer Research (IPR), Department of Chemical
Engineering, University of Waterloo, Waterloo,
Ontario N2L 3G1, Canada

E. Vivaldo-Lima
Facultad de Química, Departamento de Ingeniería Química,
Universidad Nacional Autónoma de México, CP 04510, Mexico,
DF, Mexico

DVB by using a different kind of initiator (TBEC) that has a lower decomposition rate, compared to BPO and AIBN. To better understand the behavior of TBEC in this system, experiments were performed at different temperatures, DVB concentrations, initiator concentrations, and molar ratios between controller and initiator.

Experimental

2,2,6,6-Tetramethyl-1-piperidinoxyl (Acros Organics, 98%), TBEC initiator (Sigma–Aldrich, 95%), and DVB (Sigma–Aldrich, 80%) were used as received. Styrene (Sigma–Aldrich, 99%) was washed thrice with a 10 w/v% sodium hydroxide solution and then thrice with deionized water. After that it was dried over calcium chloride and distilled under vacuum. Desired quantities of styrene, DVB, initiator, and controller were weighed, mixed, and then placed into ampoules. These ampoules were degassed by at least three freeze/pump/thaw cycles under vacuum in order to remove oxygen. After torch-sealing, the ampoules were placed into an oil bath at controlled temperature. Ampoules were withdrawn at pre-set times, temporarily placed inside a bath with ice, and then in a bath with liquid nitrogen to stop the reaction. The ampoules were weighed, broken, and the polymer/monomer mixture was first dissolved in methylene chloride, and then precipitated with ethanol. After evaporation of solvent and monomer, monomer conversion was obtained gravimetrically. The polymer molecular weights were characterized by a Viscotek TDA 302 gel permeation chromatograph (GPC) with a triple detector (viscometer, right-angle laser light scattering (RALLS), and refractive index (RI)). The chromatograph was equipped with one Viscogel precolumn from Viscotek and two Viscogel I-MBHMW-30783 columns (limit of exclusion 10MK) with dimensions of 300 mm (length) × 7.8 mm (inside diameter), with particle size of 10 μm. Filtered and degassed tetrahydrofuran (THF) (Fischer Chemical) was used as eluent at a flow rate of 1 mL/min. The samples were dissolved in THF to obtain concentrations of 1 mg/mL, and the injection volume used was 100 μL. A specific refractive index increment (d*n*/d*c*) of 0.185 mL/g was used in the calculations.

For the experiments, a factorial design was used, based on four factors (temperature (*T*), initiator concentration (*I*), weight fraction of DVB (wt DVB), and [TEMPO]/[TBEC] molar ratio, which will be denoted as *R* from now on) and three centre points. Two levels were used for each factor and hence 19 runs were conducted, as shown in Table 1. The last three runs (17, 18, and 19) are independent replicates at the centre point.

Results and discussion

In this section, only selective runs from the ones cited in Table 1 will be discussed, for the sake of brevity.

Table 1 Summary of experimental conditions for NMRP 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

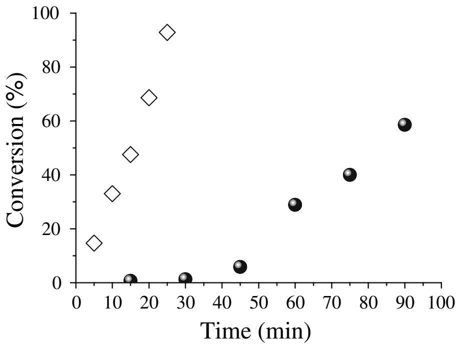

Fig. 1 Conversion versus time profiles, considering controlled and standard copolymerization of styrene and divinylbenzene at $T = 125$ °C, [TBEC] = 0.036 mol/L, mass fraction of DVB = 1%. *Filled circle* indicates controlled polymerization—R-1.1, *open diamond* indicates standard polymerization

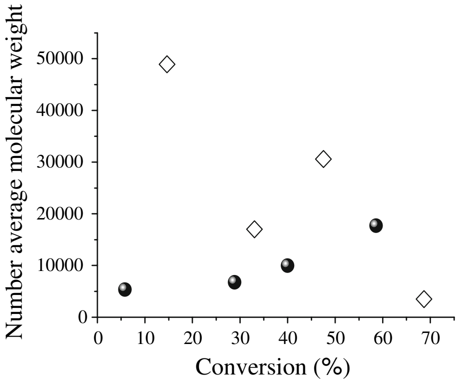

Fig. 2 Number average molecular weight versus conversion profiles, considering controlled and standard copolymerization of styrene and divinylbenzene at $T = 125$ °C, [TBEC] = 0.036 mol/L, mass fraction of DVB = 1%. *Filled circle* indicates controlled polymerization—R-1.1, *open diamond* indicates standard polymerization

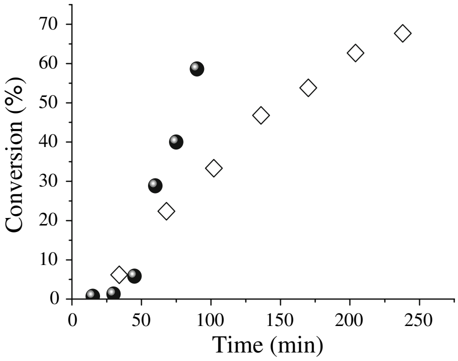

Fig. 3 Effect of the increase of TBEC and TEMPO concentrations on the rate of polymerization at $T = 125$ °C. [TEMPO]/[TBEC] = 1.1, mass fraction of DVB = 1%. *Filled circle*—[TBEC] = 0.036 mol/L, *open diamond*—[TBEC] = 0.0029 mol/L

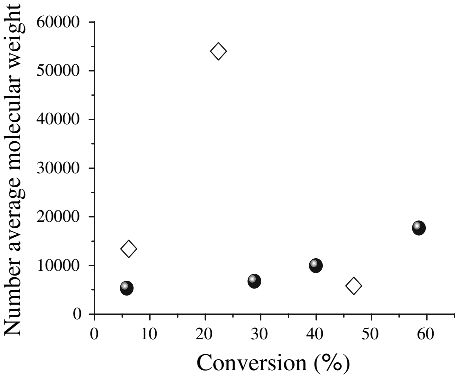

Fig. 4 Effect of the increase of TBEC and TEMPO concentrations on the number average molecular weight at $T = 125$ °C, [TEMPO]/[TBEC] = 1.1, mass fraction of DVB = 1%. *Filled circle*—[TBEC] = 0.036 mol/L, *open diamond*—[TBEC] = 0.0029 mol/L

Figures 1 and 2 show conversion and number average molecular weight profiles, respectively, considering controlled and standard polymerizations of styrene with DVB at 125 °C. Both cases used a TBEC concentration of 0.036 mol/L and a DVB mass fraction of 1%. Figure 1 shows that the standard polymerization is almost five times faster than the controlled case. Regarding molecular weight development, the number average molecular weights obtained in the NMRP process were low (less than 20,000 around 60% conversion) and increased in a controlled (linear) way, compared to the standard polymerization which yielded values of number average molecular weight shooting up to about 50,000 at 15% conversion. In addition, the standard polymerization exhibited gel formation at conversions around 15%, whereas, in contrast, gel formed at about 60% conversion in the NMRP case. After gel formation (and throughout this paper in analogous situations), the measured molecular weights in the standard polymerization decreased, because only the sol fraction was measured in the GPC.

In Figs. 3 and 4, the effect on rates and molecular weight development, respectively, of a simultaneous increase in TEMPO and initiator concentrations (keeping the molar ratio between them equal to 1.1, temperature of 125 °C and mass fraction of DVB equal to 1%) is shown. As expected, Fig. 3 shows that a significant increase in polymerization rate occurs when higher concentrations of initiator and controller are used. This occurs because for the runs with higher concentrations, more free radicals are generated, increasing the propagation rate in between the cycles of radical activation-deactivation. Figure 3 also shows that when higher concentrations of controller and initiator are used, an increase in the induction period, which is the time needed for the equilibrium between dormant and active species, is observed. This fact can be explained by the influence of the free radicals generated by the thermal initiation of styrene on the system with lower initiator (0.0029 mol/L) and TEMPO (0.00319 mol/L) concentration, increasing total radical concentration. This way, a larger radical generation could decrease the molar ratio between controller and initiator in the system with lower initiator and controller concentration. In a system with lower molar ratio, a larger concentration of generated radicals will take less time to react reversibly with nitroxide radicals, generating dormant molecules. For the system with higher initiator and controller concentrations (by 12 times), additional free radicals are also produced by thermal initiation of styrene, but their effect is less pronounced. Figure 4 shows advantages in using higher concentrations of initiator and controller, as it is possible to obtain more controlled polymer at a faster polymerization rate (see Fig. 3). When the concentration of TBEC was equal to 0.0029 mol/L, the gelation point occurred at around 20% monomer conversion (maximum molecular weight). For higher initiator and controller concentrations, the gelation point occurs later, at conversion around 60%. This happens because when higher concentrations of controller are used, the polymer chains are smaller since development of MW in a controlled radical process is inversely proportional to the controller concentration. This is due to the increase in TEMPO, which results in less polymer radicals [1].

The effect of temperature on conversion and number average molecular weight is shown in Figs. 5 and 6, respectively. An increase of 10 °C in temperature causes a significant acceleration in rate (see Fig. 5), not only because temperature causes an increase in polymerization (propagation) and initiation rates (chemical and thermal) but also because it increases the activation rate constant, causing an increase in the active radical concentration. Figure 5 also shows a reduction in the induction period when working at higher temperature, due to the increase of the initiator decomposition rate constant and of the thermal initiation. Both mechanisms generate more radicals at the beginning of the polymerization. These free radicals react with the excess of TEMPO present in the system, since the ratio between controller and initiator used in this case is 1.4, somewhat higher than the ratio usually employed in typical controlled polymerizations. It can also be seen that for both temperatures, the time required to reach high conversion is considerably short, because the free radicals are produced much more slowly when using TBEC, a situation analogous to the case of thermal initiation [9]. In Fig. 6 the measured values of number average molecular weight are very close for both temperature levels, in agreement with what was observed by Nabifar et al. [12] for controlled homopolymerization of styrene. In both cases of Fig. 6, the gelation point occurred at conversions around 50%.

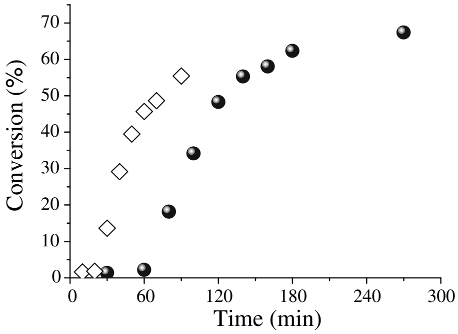

Fig. 5 Effect of temperature on the rate of polymerization at [TBEC] = 0.036 mol/l, [TEMPO]/[TBEC] = 1.4, mass fraction of DVB = 1%. *Filled circle*—$T = 125$ °C, *open diamond*—$T = 135$ °C

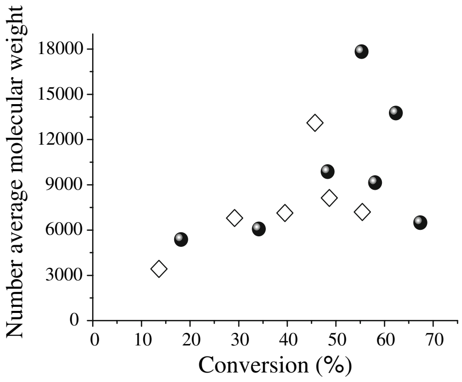

Fig. 6 Effect of temperature on the number average molecular weight at [TBEC] = 0.036 mol/L, [TEMPO]/[TBEC] = 1.4, mass fraction of DVB = 1%. *Filled circle*—$T = 125$ °C, *open diamond*—$T = 135$ °C

Figure 7 shows the molecular weight distribution profile for a selected sample from run 8, at 135 °C, for a conversion level of 30%. A well behaved and symmetrical profile (showing a controlled process) can be observed, with PDI equal to 1.3. For standard polymerizations (Figs. 1, 2), the gelation point occurred before 15% conversion. In contrast, as observed in Fig. 7, in the polymerization using TBEC it is possible to reach 30% conversion and obtain a controlled polymer (PDI = 1.3), while the gelation point occurs in this system at around 50% conversion.

Figure 8 shows the PDI profile at the operating conditions presented in Fig. 7. The low PDI values suggest that the polymer is more homogeneous, with probably less intrachain crosslinks. Figure 5 showed that 50% of monomer conversion could be reached in just about one hour of reaction, which is a short period of reaction time when dealing with a NMRP process. Table 2 shows a comparison between TBEC and BPO in the copolymerization of styrene and DVB with initiator concentration equal to

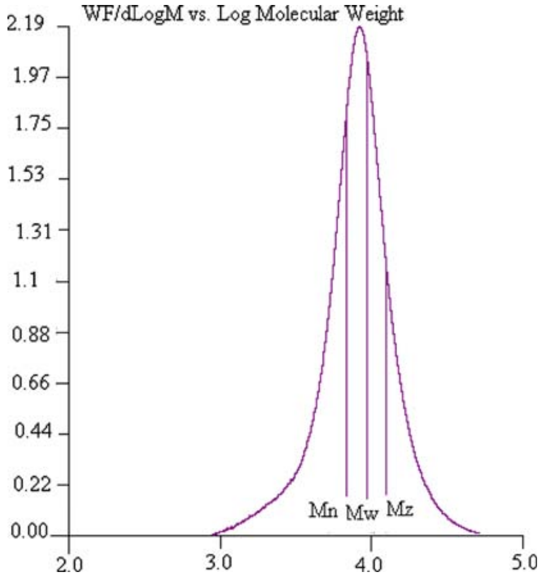

Fig. 7 Molecular weight distribution obtained by GPC at a conversion of 30% and $T = 135$ °C, $R = 1.4$, [TBEC] = 0.036 mol/L and mass fraction of DVB = 1.0%

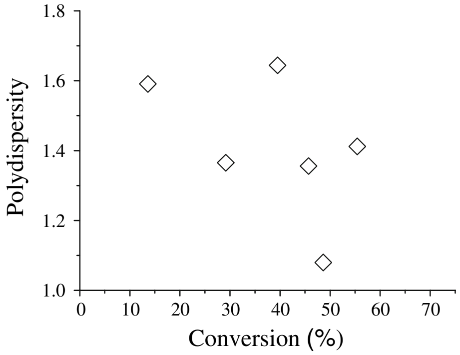

Fig. 8 Polydispersity versus conversion profile at [TBEC] = 0.036 mol/L, [TEMPO]/[TBEC] = 1.4, mass fraction of DVB = 1%, $T = 135$ °C

Table 2 Time needed to reach monomer conversion of 40% with TBEC and BPO initiators

	Temperature (°C)	Time (min)
BPO[a]	120	600
BPO[a]	130	342
TBEC	125	108
TBEC	135	50

Conditions of the copolymerization: $[I] = 0.036$ mol/L, $R = 1.4$ and mass fraction of DVB = 1%

[a] Experimental results obtained from our group

0.036 mol/L, molar ratio between TEMPO and initiator equal to 1.4, and mass fraction of DVB equal to 1%. For all the cases of Table 2, the time needed to reach monomer conversion equal to 40% was recorded. One can see a significant reduction in polymerization time when TBEC is used as initiator.

The effects of the [TEMPO]/[TBEC] molar ratio on polymerization rate, number average molecular weight, and polydispersity are shown in Figs. 9, 10, 11, respectively. It can be observed that an increase in the TEMPO concentration, while maintaining the same initiator concentration, i.e., an increase in the molar ratio, caused a decrease in the rate of polymerization and an increase in the induction period (see Fig. 9). This is in agreement with what was discussed before, in relation to the balance between radicals and controller (Fig. 5). At the same time, it is observed from Figs. 10 and 11 that only slightly lower molecular weight and polydispersity values are obtained when using more TEMPO (i.e., higher ratio).

Figures 12 and 13 show the effect of DVB content on polymerization rate, considering four different experimental conditions (runs 1, 7, 9, and 15 of Table 1). These results show that the weight fraction of DVB, at least at the

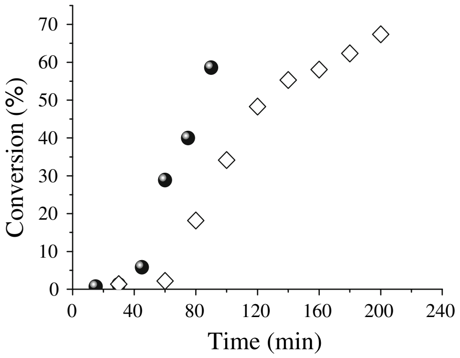

Fig. 9 Effect of molar ratio of [TEMPO]/[TBEC] on rate of polymerization at $T = 125$ °C, [TBEC] = 0.036 mol/L, mass fraction of DVB = 1%. *Filled circle*—molar ratio = 1.1, *open diamond*—molar ratio = 1.4

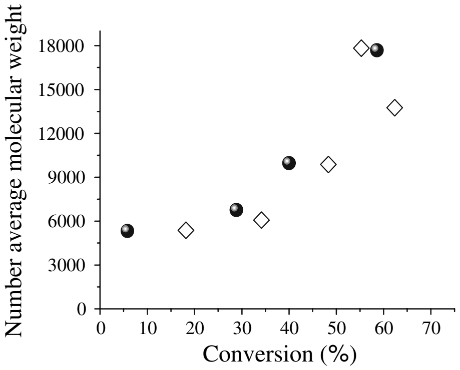

Fig. 10 Effect of molar ratio of [TEMPO]/[TBEC] on number average molecular weight at $T = 125$°C, [TBEC] = 0.036 mol/l, mass fraction of DVB = 1%. *Filled circle*—molar ratio = 1.1, *open diamond*—molar ratio = 1.4

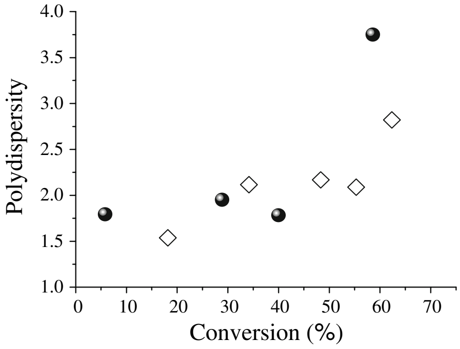

Fig. 11 Effect of molar ratio of [TEMPO]/[TBEC] on polydispersity at $T = 125°C$, [TBEC] = 0.036 mol/L, mass fraction of DVB = 1%. *Filled circle*—molar ratio = 1.1, *open diamond*—molar ratio = 1.4

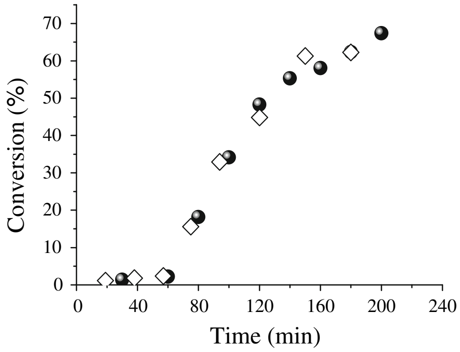

Fig. 12 Effect of the weight fraction of DVB on rate of polymerization at $T = 125$ °C, [TEMPO]/[TBEC] = 1.4, [TBEC] = 0.036 mol/L. *Filled circle*—wt DVB = 1%, *open diamond*—wtDVB = 1.5%

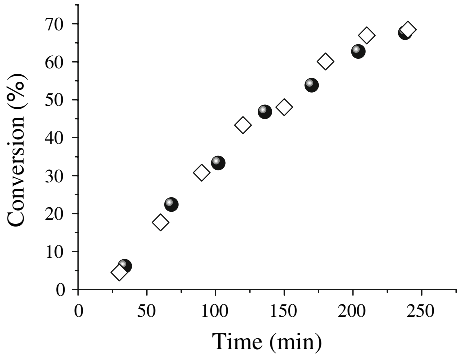

Fig. 13 Effect of the weight fraction of DVB on rate of polymerization at $T = 125°C$, [TEMPO]/[TBEC] = 1.1, [TBEC] = 0.0029 mol/L. *Filled circle*—wt DVB = 1%, *open diamond*—wt DVB = 1.5%

levels used herein, has a low influence on the rate of polymerization, in agreement again with what was reported previously in Tuinman et al. [3] with BPO initiator. In the same way, no significant differences were observed on molecular weights, when changing the weight fraction of DVB, for runs with a similar gelation point.

Table 3 Effects of studied factors on variables of interest

	Conversion	Molecular weights	Poydispersity
↑ Molar ratio [TEMPO]/[TBEC]	↓	$^{\downarrow}$	$^{\downarrow}$
↑ Temperature	↑	—	—
↑ TBEC and TEMPO concentration	↑	↓	↓
↑ Divinylbenzene concentration	—	—	—

↑ increase; ↓ decrease; $^{\downarrow}$ slight decrease; — no detectable effect

Finally, Table 3 shows a summary of the effects of the studied factors (temperature, molar ratio of [TEMPO]/[TBEC], TEMPO and TBEC concentrations, and DVB concentration) on conversion, molecular weight averages, and polydispersity values. It is observed that an increase in the TEMPO/TBEC ratio caused a decrease on conversion, number average molecular weights, and polydispersity. The effect on monomer conversion was the most significant. An increase in temperature had practically no effect on the properties of the polymer (PDI and MWs), but it directly affected polymerization rate. When increasing both TBEC and TEMPO concentrations, keeping constant the ratio between them, a reduction in molecular weights and polydispersity, and an increase in conversion, is observed. Finally, no detectable effect was observed on conversion, molecular weights, and polydispersity when changing the concentration of DVB.

Conclusions

A comprehensive experimental study on the use of TBEC in the bimolecular NMRP of styrene with DVB was carried out. It was found that polymerization with TBEC was indeed controlled and faster when compared to the one obtained with BPO. The generated polymer networks seemed more homogeneous, when compared to those obtained with standard copolymerizations.

Acknowledgements The authors would like to acknowledge the financial support from FAPESP, CAPES and CNPq (Brazil), CONACYT (Project CIAM U40259-Y) (Mexico), and NSERC/CRO/CRC (Canada), for a special Inter-American Materials Collaboration (IAMC or CIAM) joint project.

References

1. Veregin R, Odell P, Michalak L, Georges M (1996) Macromolecules 29:4161

2. Roa-Luna M, Nabifar A, McManus NT, Lima EV, Lona LMF, Penlidis A (2008) J Appl Polym Sci 109:3665
3. Tuinman E, McManus N, Roa-Luna M, Vivaldo-Lima E, Lona L, Penlidis A (2006) J Macromol Sci A 43:995
4. Butté A, Storti G, Morbidelli M (1999) Chem Eng Sci 54:3225
5. He J, Chen J, Li L, Pan J, Li C, Cao J, Tao Y, Hua F, Yang Y, Mckee G, Brinkmann S (2000) Polymer 41:4573
6. Díaz-Camacho F, López-Moralez S, Vivaldo-Lima E, Saldívar-Guerra E, Vera-Graziano R, Alexandrova L (2004) Polym Bull 52:339
7. Dias R, Gonçalves M, Lona L, McManus N, Vivaldo-Lima E, Penlidis A (2007) Chem Eng Sci 62:5240
8. Goto A, Fukuda T (1997) Macromolecules 30:4272
9. Greszta D, Matyjaszewski K (1997) J Polym Sci A 35:1857
10. Ide N, Fukuda T (1999) Macromolecules 32:95
11. Tsoukatos T, Pispas S, Hadjichristidis N (2001) J Polym Sci A 39:320
12. Nabifar A, McManus N, Vivaldo-Lima E, Lona L, Penlidis A (2008) Can J Chem Eng 86:879