Controlled Free-Radical Copolymerization Kinetics of Styrene and Divinylbenzene by Bimolecular NMRP using TEMPO and Dibenzoyl Peroxide

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An experimental study on the kinetics of nitroxide-mediated free radical copolymerization (NMRP) of styrene (STY) and divinylbenzene (DVB) is presented. The experiments were carried out in bulk from a mixture of monomers, stable free radical controller (2,2,6,6-Tetramethyl-1-piperidinyloxy, TEMPO), and initiator (dibenzoyl peroxide, BPO), at 120°C, without using a TEMPO-capped prepolymer in the initial mixture. The system studied is a case of bimolecular NMRP, as opposed to the monomolecular NMRP of styrene and other crosslinker previously addressed in the literature by others. The results on total monomer conversion (polymerization rate), molecular weight development, gel fraction, and swelling index are compared against a conventional reference system (a STY/DVB copolymer, also synthesized for this study). No significant auto-acceleration effect was observed in the early and intermediate conversion ranges of the TEMPO-controlled copolymerization of STY/DVB, and the gelation point was significantly delayed.

Keywords copolymerization, crosslinking, living free radical polymerization, nitroxide mediated free radical polymerization, TEMPO, styrene-divinylbenzene

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Introduction

The so called controlled/"living" free-radical polymerization (CRP) has been the subject of much research over the past few years (1). There are three main types of reaction covered under this general heading: atom transfer radical polymerization (ATRP), reversible addition-fragmentation transfer polymerization (RAFT), and nitroxide mediated radical polymerization (NMRP). All these processes have one common theme, which is the presence in the polymerization mechanism of a reversible radical generation (degradation) step, used to control the effective concentration of radicals in the polymerization medium.

Each type has its own strengths and drawbacks. ATRP is very versatile in terms of applicability to different monomer systems, but relies on the activity of metal catalysts to control the reaction. This can cause difficulty in terms of product work up, to produce polymer with low levels of metal residue. RAFT is again very versatile but the controlling agents are difficult to obtain. NMRP is based around stable aminoxyl (nitroxyl) radicals, which are easy to handle but show their best performance with mostly styrenic monomers. NMRP processes have the positive feature that they give products with low polydispersity index (PDI) values, sometimes achieving PDI as low as 1.1, but typically lead to slow polymerizations and for most conditions cannot reach 100% monomer conversion. A common drawback of all CRP processes is the fact that high molecular weight product with good mechanical properties is usually not attainable. Therefore, the main potential applications are related to synthetic steps in the production of polymeric materials of complicated architectures (e.g., block and graft copolymers, stars, less heterogeneous polymer networks, etc.).

Crosslinked polymers (polymer networks) are very important in technology, medicine, biotechnology, agriculture, and other areas. They are used as construction materials, paints and coatings, polymer glasses with high mechanical strength and high thermal stability, rubbers, ion-exchange resins and sorbents, insoluble polymer supported reagents, controlled drug-release matrices, electronics and cables, food packaging, sensors, "smart" materials, artificial organs, implants, superabsorbent materials, etc. Poly(styrene-co-divinylbenzene) is a crosslinked polymer used for chromatographic applications and as precursor for ion-exchange resins, among other uses. It is also a model system in the study of network formation via crosslinking free-radical copolymerization. Most applications of polymer networks require a homogeneous structure to obtain optimal performance. However, the polymer networks obtained by free-radical copolymerization are rather heterogeneous in nature. It would be desirable to have a synthetic route to synthesize homogeneous polymer networks with free radical technology. This goal might, in principle, be possible to achieve by copolymerizing vinyl and divinyl monomers in the presence of CRP controllers.

The synthesis, characterization and modeling of polymer networks by CRP processes are research areas where few reports are available in the open literature. To our knowledge, the first paper reporting the synthesis of a microgel from tert-butylstyrene and 1,4-divinybenzene, in the presence of a NMRP synthesized aminoxy-terminated poly(tert-butylstyrene), came from Solomon and coworkers (2, 3). At about the same time, Ide and Fukuda (4, 5) presented more detailed reports on the copolymerization of styrene and small amounts of 4,4′-divinylbiphenyl, in the presence of an oligomeric poly-styryl adduct (2,2,6,6-tetramethylpiperidivinyl-1-oxy, PS-TEMPO), at 125°C, and evaluated the pendant vinyl reactivity (4), and the gelation behavior (5) of the system. The two reacting systems mentioned before (2–5) used nitroxyl-capped oligomers as controlling agents, thus constituting monomolecular NMRP processes. Asgarzadeh et al. (6) produced polymer networks by synthesizing a difunctional precursor by ATRP and using

the end-linking process (reactions between difunctional precursors and crosslinking agents). The group of Fréchet (7, 8) reported a solution copolymerization of styrene and divinylbenzene, in the presence of TEMPO (7) and other more effective NMRP controllers (8), to produce poly(styrene-co-divinylbenzene) monoliths for direct use in chromatographic applications. Ward and Peppas (9) modeled the INIFERTER (the same controller molecule acting as initiator, chain transfer agent, and terminator) controlled free radical copolymerization of vinyl-divinyl monomers, using the percolation theory. Yu et al. (10) reported an experimental study on the ATRP of poly(ethylene glycol) dimethacrylate (PEGDMA), initiated by an alkyl halide, and compared their results of polymerization rate and gel formation against a reference conventional system. Barner et al. (11) carried out the RAFT grafting with polystyrene of core poly(divinylbenzene) beads, but also included in their study is the production of core poly(divinylbenzene) in the presence of RAFT agent 1-phenylethyl dithiobenzoate (PEDB) by precipitation polymerization. Norisuye et al. (12) carried out a comparative study between conventional and RAFT controlled free-radial copolymerization of styrene and divinylbenzene, starting from monomers, and not from the prepolymer. They used time-resolved laser light scattering and gel permeation chromatography to perform their study, concluding, as Ide and Fukuda did for NMRP (4, 5), that more homogeneous polymer networks are possible by using CRP methods. Zetterlund et al. (13) reported the nitroxide-mediated controlled radical copolymerization of styrene and divinylbenzene, at 125°C, using a polystyrene-TEMPO macroinitiator in bulk and in aqueous mini-emulsion, observing significant differences in the polymerization rate and crosslink density, depending on the reaction medium. Hirano et al. (14) studied the polymerization of DVB in the presence of nitrobenzene as a retarder, using an excess of dimethyl 2,2′-azobisisobutyrate (MAIB) to promote the formation of hyperbranched structures, at 70 and 80°C. Based on the kinetic equation that describes the initial polymerization rate, they found, at 70°C that the radicals coming from the nitro group of nitrobenzene behave as a NMRP controller, forming dormant polymer molecules.

The objective of the work described herein was to examine the polymerization of styrene and divinylbenzene at elevated temperatures (higher than 100°C) with and without TEMPO, and using BPO as an initiator (bimolecular NMRP, as opposed to the monomolecular NMRP copolymerization of vinyl/divinyl monomers previously studied by others (2–5)). The motivation for this study was twofold. Firstly, to examine the nitroxide controlled radical polymerization in the presence of small amounts of crosslinking agent. This was to see if it led to any changes in kinetic behavior that could relate to viscosity increases, which would cause diffusion-controlled effects analogous to those seen in conventional free radical polymerizations at high monomer conversions, and those proposed in the Vivaldo-Lima group (15, 16) to explain the loss of livingness of CRP processes at high conversions (and the significant acceleration in polymerization rate apparently caused by the intermittent semi-batch addition of an initiator in NMRP of styrene (17)). The second motivation was to start exploratory work on the effect of CRP on the homogeneity of the produced polymer network, since there is some disagreement in the literature about this issue, with some researchers arguing that the produced polymer networks are more homogeneous when CRP is used to synthesize them (4, 5, 12), whereas others claim that the only effect is to delay gelation, without any significant effect on the homogeneity of the polymer network (9).

In order to analyze the experimental data from copolymerization of STY/DVB in the presence of TEMPO and BPO, at 120°C, two reference systems were considered. One was the bimolecular nitroxide mediated radical homopolymerization of styrene using TEMPO

and BPO, at 120°C, and the other was the conventional copolymerization of STY/DVB at 125°C, using di-tert-butyl peroxide (Trigonox B) as the initiator. The conventional homo-polymerization of styrene with Trigonox B, at 125°C, was also included in the study, for comparison purposes.

Experimental

Materials and Polymerization Technique

Styrene (STY) and divinylbenzene were obtained from Aldrich. The DVB was a technical mixture of isomers, with approximately 80% of DVB. Styrene was washed three times with a NaOH solution and dried over anhydrous $CaCl_2$, and then distilled in vacuum to remove the inhibitor and impurities. Di-tert-butyl peroxide (Trigonox B, AKZO chemicals) and dibenzoyl peroxide (97%, Aldrich) were used as received. TEMPO (99%, purified by sublimation) was also obtained from Aldrich, and used as received. The solvents (acetone, chloroform, ethanol, tetrahydrofuran (THF), dichloromethane, toluene, and petroleum ether) were used as received from BDH.

The homo- and co-polymerizations were carried out in sealed ampoules of 5 mm inner diameter and approximately 25 cm in length. The mixture contents were added to the ampoules. After degassing by four successive freeze–thaw cycles using liquid nitrogen and a reduced pressure (approximately 10^{-4} torr), the ampoules were torch sealed. The polymerization was initiated by immersing the ampoules in a silicone oil bath maintained at the designated temperature (see Table 1). The polymerization was stopped by inserting the ampoules into liquid nitrogen. Once opened by using a glass cutter, the reaction mixture was transferred into a flask with dichloromethane, containing hydroquinone to inhibit further reaction. After dissolving in dichloromethane, the polymer was precipitated with ethanol, left in air flow for one day, and then dried in a vacuum oven until constant weight was obtained.

Polymer Characterization

Total monomer conversion was obtained gravimetrically. Products were characterized for molecular weight (averages and molecular weight distribution) by using a size exclusion chromatograph (SEC or GPC). The SEC equipment consists of a Waters solvent delivery system and autosampler followed by Viscotek's quad detector equipped with a UV detector, low- and right-angle laser light scattering detectors (LALLS/RALLS), differential refractometer and viscometer in the series. One PLgel 10 μm guard column (50×7.5 mm, Polymer Laboratories Ltd.) and three HR 5E columns (300×7.5 mm, Waters) were used with the detectors and columns maintained at 30°C. The laser operated at 670 nm and the light-scattering intensity was measured at 7° (LALLS) and 90° (RALLS). Data analysis for this system was performed using an OmniSEC version 3.0 (Viscotek).

Tetrahydrofuran (THF) (Caledon Laboratories Inc.) was filtered and used as the eluent at a flow rate of 1 mL/min for the SEC setup. The polymer was dissolved in THF to obtain concentrations of ∼0.2 wt% and the injection volume varied between 100 and 200 μL. The second virial coefficient for the light-scattering equation was assumed to be negligible as very low concentrations of polymer were employed. A specific refractive index increment (dn/dc) value of 0.185 mL/g was used in the light scattering analysis for PS (polystyrene).

Gel content (gel fraction and swelling index) for the samples (toluene insoluble polymer) was measured using the ASTM method D3616-95.

Table 1
Experimental plan

Run	Type[a]	Monomer	Temperature (°C)	Feed details
1	Conventional free radical	Styrene	125°C	Bulk sty, Trig B (0.006M)
2	NMRP	Styrene	120°C	Bulk sty, BPO (0.0355M), TEMPO (0.0396M)
3	Conventional free radical	Styrene/DVB	125°C	Bulk sty, 1 wt% DVB, Trig B (0.006M)
4	NMRP	Styrene/DVB	120°C	Bulk sty, 1 wt% DVB, BPO (0.03605M), TEMPO (0.03961M)
5	NMRP Extended reaction period	Styrene	120°C	Bulk sty, BPO (0.0355M), TEMPO (0.0396M)
6	NMRP	Styrene/DVB	120°C	Bulk sty, 1.5 wt% DVB, BPO (0.03599M), TEMPO (0.03959M)
7	NMRP	Styrene/DVB	120°C	Bulk sty, 2.99 wt% DVB, BPO (0.0360M), TEMPO (0.03962M)
8	NMRP Repeat at UNAM	Styrene	120°C	Bulk sty, BPO (0.0355M), TEMPO (0.0396M)

[a]NMRP: nitroxide mediated radical polymerization.

Polymerization Conditions

Eight runs were carried out for the kinetic study. The first run was a reference case of conventional STY homopolymerization, at 125°C, using Trigonox B as initiator. The second run was a NMRP of STY, at 120°C, using BPO and TEMPO at a molar ratio of TEMPO/BPO = 1.1. The third run was a conventional copolymerization of STY and DVB, using Trigonox B. Runs 4, 6 and 7 were NMRP copolymerizations of STY and DVB at the same molar ratio of run 2, but using different amounts of DVB. Run 5 was a NMRP of STY with the same conditions of run 2, but with sampling at later times, aiming at reaching higher

conversions. Run 8 was a repeat of runs 2 and 5, carried out in a different lab (Faculty of Chemistry of the National Autonomous, University of Mexico, UNAM). The details of the formulations and operating conditions are shown in Table 1.

Results and Discussion

As explained before, the approach followed in our study was to first look at the conventional homopolymerization of styrene, as a reference for comparison with the other cases. We felt this step was necessary because the copolymerization of STY/DVB was done at a higher temperature than reported in the literature. The next step in our approach consisted of carrying out NMRP of styrene with TEMPO, to serve as a comparison for the final step of the study, which was to examine the copolymerization of STY and DVB in the presence of TEMPO, namely, to carry out bimolecular nitroxide mediated radical copolymerization of vinyl/divinyl monomers.

Conventional Free Radical Polymerization of Styrene and Copolymerization of Styrene/Divinylbenzene

Figure 1 shows a comparison of the polymerization rate, expressed as conversion vs. time, between a conventional homopolymerization of STY at 125°C, using Trigonox B as initiator at a concentration of 0.006 M, and its corresponding copolymerization with DVB at a concentration of 1 wt%. As expected, the polymerization proceeds faster when a small amount of DVB is added to the reaction mixture. The faster polymerization
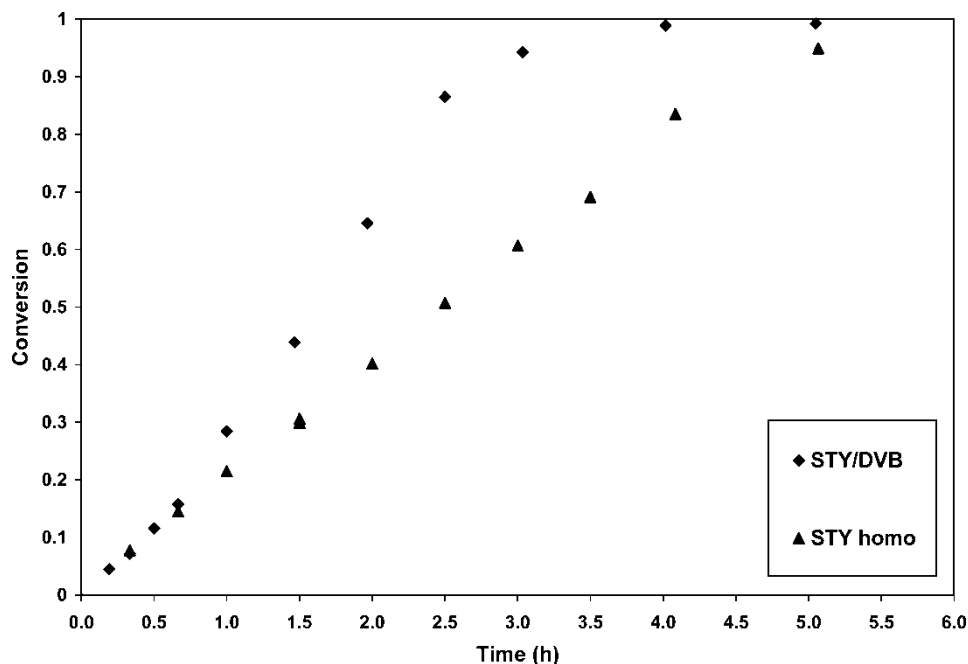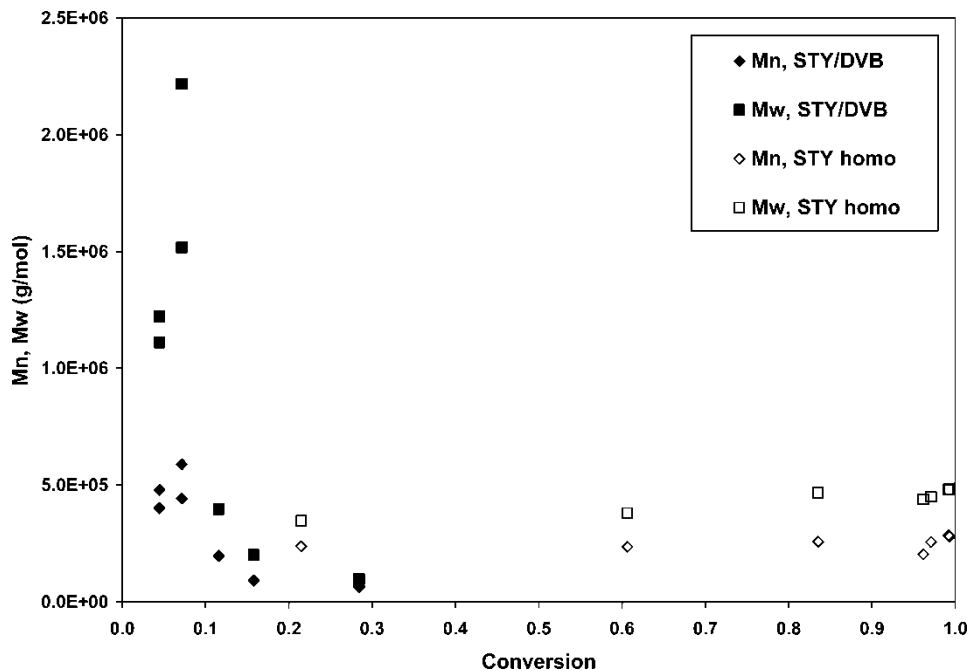

Figure 1. Comparison of experimental polymerization rates in the conventional free radical homopolymerization of STY and copolymerization of STY/DVB at the conditions of runs 1 and 3 (Table 1), respectively.

rate is caused by a combined effect of having two reactive double bonds per DVB monomer unit (making its polymerization rate close to twice the polymerization rate of a single STY monomer unit), and more importantly the fact that the production of a three-dimensional polymer network causes viscosity to increase much faster and to much higher values than the linear homopolymerization case. Thus, diffusion-controlled termination (the so-called auto-acceleration or gel effect) causes the polymerization rate to proceed significantly faster in the copolymerization.

Figure 2 shows a comparison of number and weight average molecular weights for the two cases studied in Figure 1, namely, runs 1 and 3 of Table 1. The expected results of number and weight average molecular weights (M_n and M_w, respectively) increasing very slowly for the homopolymerization case, and M_w increasing towards very large values at the gelation point in the copolymerization of STY/DVB, are clearly observed. The fast decrease of the values of M_n and M_w with conversion during the post-gelation period shows a fast consumption of the sol polymer molecules being converted into gel, typical of standard vinyl/divinyl copolymerizations.

Figure 3 shows experimental data of gel content vs. conversion. It is clearly observed that gelation takes place at about 7% monomer conversion. Sol is converted into gel very rapidly, reaching 70% gel content at about 11% monomer conversion (approximately 20 min of polymerization time, as observed from Figure 1). Thereafter, the production of sol into gel proceeds less rapidly, but at about 45% monomer conversion (approximately 1.5 h of polymerization time), most of the polymer present in the system is gel, with the remaining monomer being swollen in the polymer network.

Figure 2. Comparison of experimental number and weight average molecular weights in the conventional free radical homopolymerization of STY and copolymerization of STY/DVB at the conditions of runs 1 and 3 (Table 1), respectively.
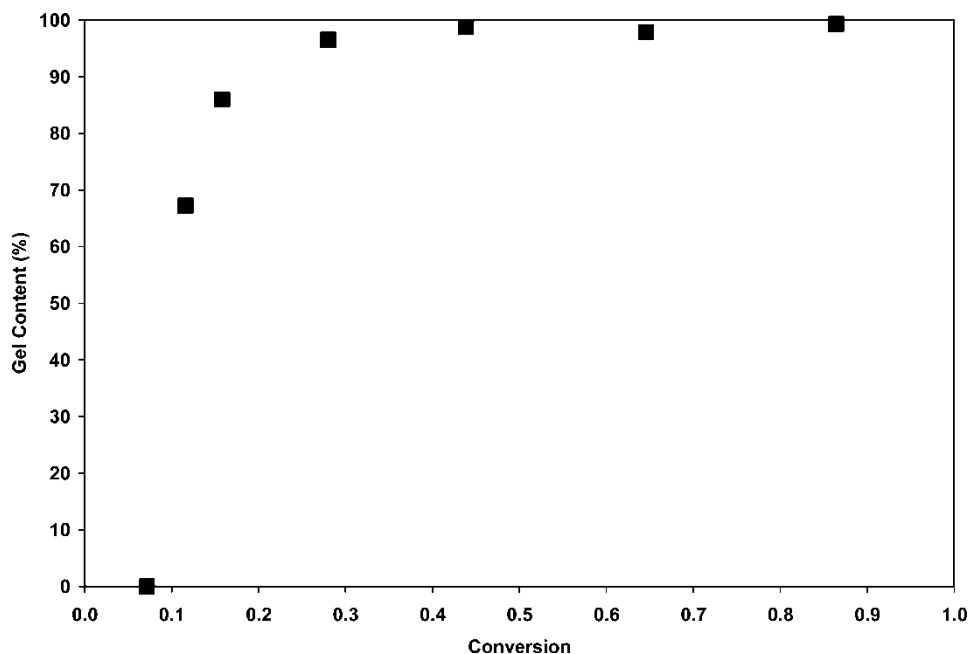
Figure 3. Gel content (percentage) evolution in the conventional free radical copolymerization of STY/DVB at the conditions of run 3 (Table 1).

Nitroxide Mediated Polymerization of Styrene and Copolymerization of Styrene/Divinylbenzene

Styrene polymerizations in the presence of TEMPO and a conventional initiator (bimolecular NMRP) have been studied for a number of years. Georges et al. (18) initiated these investigations and have since produced many studies examining specific aspects of NMRP. However, despite the numerous studies carried out, there is still a limited amount of data reported that may be used as a base for a comprehensive kinetic modeling study (see, for instance, Zhang and Ray (19), and Bonilla et al. (20)).

The initial study of NMRP of STY in this work was done using BPO and TEMPO levels that had been reported previously in the literature, with the aim of expanding the data set and confirming that the experimental part is reproducible. The data generated here were also obtained with the aim of producing adequate experimental data for future modeling studies from our group. The conditions used for the NMRP of STY of this study are indicated in Table 1 with runs 2, 5 and 8. Experiment 5, a replicate study of 2, was done to determine conversion levels over very long reaction periods. Experiment 8, also a replicate of experiment 2, was carried out in a different lab, to obtain an even better idea of the reproducibility of our data. The results of these experiments are shown in Figures 4 and 5.

The data for conversion vs. time are quite distinct from those seen for conventional free radical polymerization of styrene at these temperatures, the most obvious feature being that the reaction rate is relatively slow, as shown in Figure 4. In run 1, complete conversion of monomer is essentially achieved after 5 h (see Figure 1), whereas for the NMRP reaction, only about 30% conversion was achieved in that time. Figure 5 shows a linear relationship between logarithmic monomer concentration and time, which is characteristic
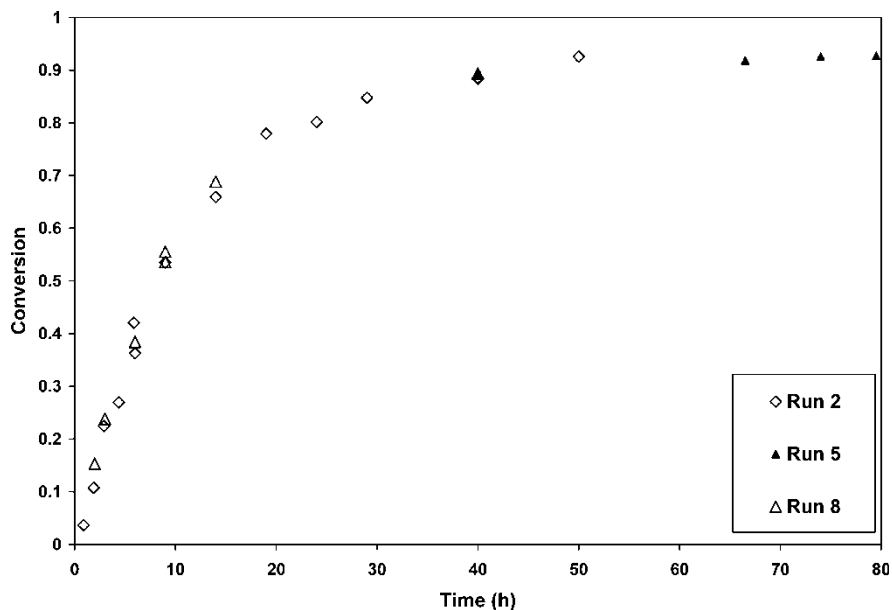
Figure 4. Experimental data of conversion vs. time for the NMRP of styrene at conditions of Table 1 (Runs 2, 5 and 8).

of a living system (although it is not a sufficient condition for livingness). It is observed that the living behavior seems to be gradually lost after about 75% monomer conversion. After that time, there is some tailing off in rate as the monomer is depleted. This again is in contrast to the conventional free radical polymerization, which shows acceleration in rate
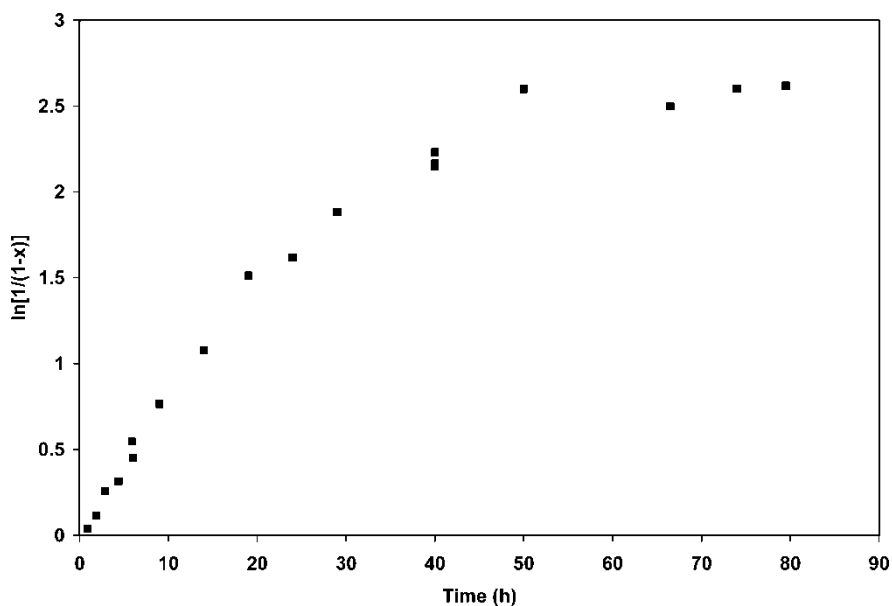

Figure 5. Experimental data of logarithmic monomer conversion vs. time for runs 2, 5, and 8.

at some point in the low or intermediate conversion ranges; this is because the equilibrium reactions of polymer radicals with TEMPO dominate over standard termination mechanisms even at high concentrations of polymer. This indicates that if there are any effects of polymer diffusion in NMRP kinetics, they are different from those observed for conventional free radical polymerization.

Molecular weight data, M_n and M_w, are shown in Figure 6. The reliability of the experimental data was confirmed in an independent replicate of the experiment. A linear relationship between M_n and conversion up to about 80% monomer conversion is observed, which serves as another indicator of living behavior of the polymerization system up to about 80%. The last two data points seem to deviate from the linear trend, gearing toward rather higher molecular weights. These could be attributed to a rather high experimental error at high conversions, or to the presence of moderate diffusion-controlled effects. The experimental weight average molecular weights (M_w) are shown in the same plot, indicating that polydispersity (PDI) is low. This is better visualized in Figure 7, where PDI is shown to vary in the range 1.05 and 1.17. Although the spread of data shown in Figure 7 could be considered random, it is interesting to note that slightly higher values of PDI are obtained in the conversion range of 0.1 to 0.65 (with the average PDI slightly higher than 1.10). Thereafter, the average PDI slightly decreases below 1.10 (around 1.07), with only one (the repeat of the last point) going back to slightly over 1.10 (PDI = 1.11). Although very subtle, this observation may be rationalized in terms of moderate diffusion-controlled (DC) effects. Delgadillo-Velázquez et al. (15) and Vivaldo-Lima and Mendoza-Fuentes (16) observed from simulation studies on ATRP and Iniferter CRP, respectively, that the combined effect of DC-termination (the so called "gel" or auto-acceleration effect), DC-propagation (glassy effect), and DC-activation/deactivation of polymer radicals, is to improve the
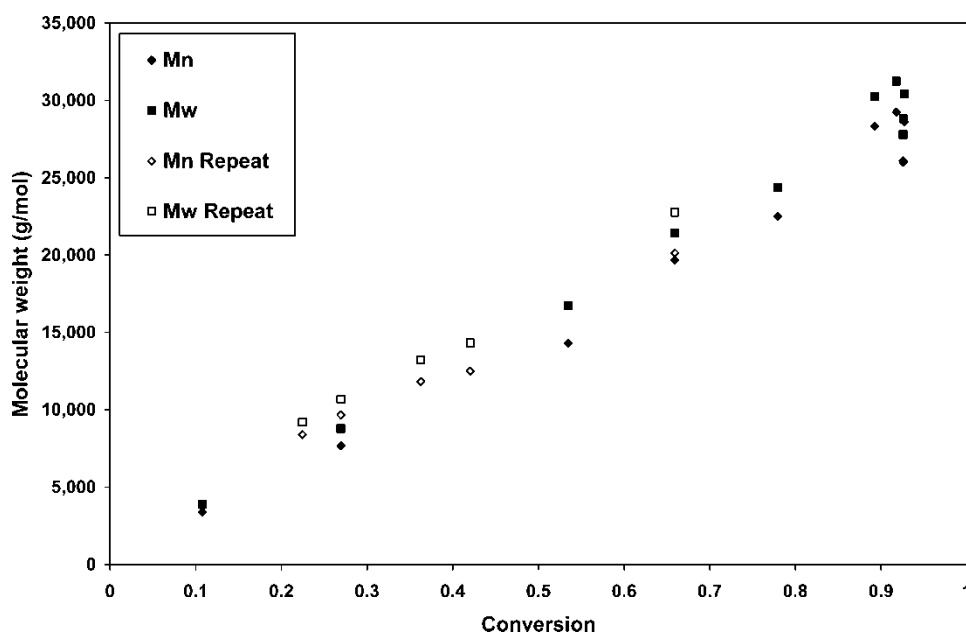
Figure 6. Experimental data of M_n and M_w vs. conversion for the NMRP of styrene at conditions of Table 1 (Runs 2 and 5).
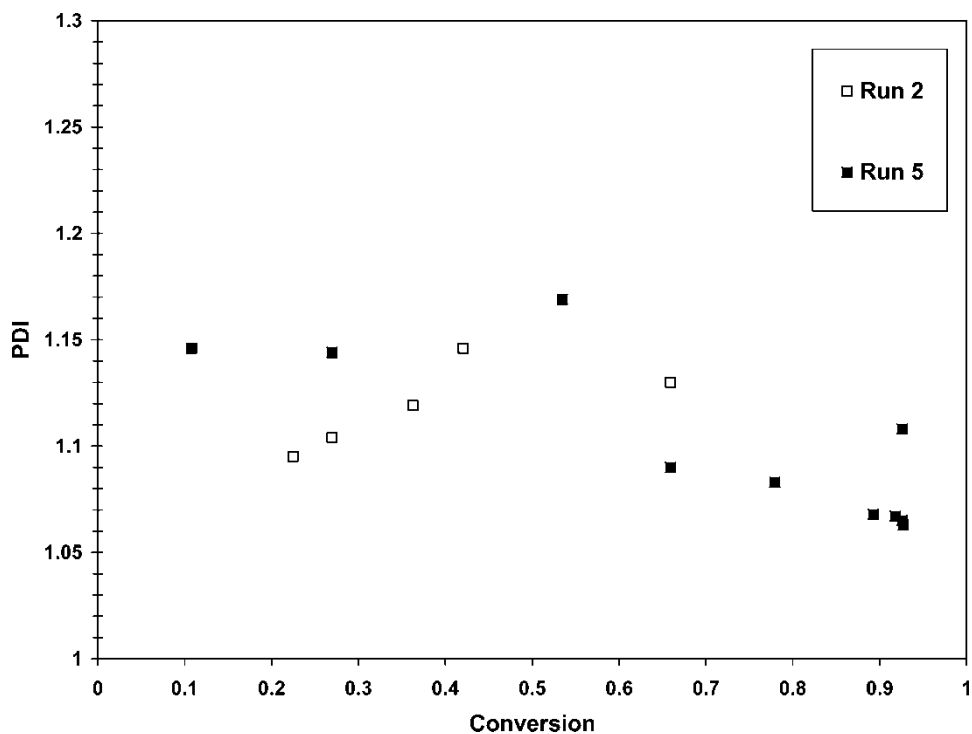
Figure 7. Experimental data of polydispersity (PDI) vs. conversion for the NMRP of styrene at conditions of Table 1 (Runs 2 and 5).

degree of livingness (measured in terms of PDI tending to become 1.0) as polymerization proceeds, during the low and intermediate conversion ranges, to be completely lost at very high conversions and approach a conventional radical polymerization behavior at those very high conversions. However, at the conditions studied here, the highest conversion obtained was 0.91, not changing from that value (reached at about 50 h of polymerization time), even after leaving the system reacting for up to 80 h. This is an issue that deserves further study, and that is why we aimed to promote higher viscosities in the system, by adding a small amount of crosslinker (DVB), with the hope of amplifying the zone where DC-effects take the system from well controlled (low PDI) to uncontrolled (PDI becoming typical of a conventional free radical polymerization).

The proposed extension was to examine the copolymerization of STY/DVB in the presence of the TEMPO/BPO initiation package. There have been reports of the use of NMRP systems in the production of microgels where it was shown that the presence of TEMPO-capped controller led to much better control in the formation of statistical microgels than that observed for conventional free radical (2, 3). Moreover, Ide and Fukuda (4, 5) have indicated the reasons for this in a study of STY copolymerization with divinyl biphenyl (DVBP) and a TEMPO-capped oligomer (monomolecular NMRP). They proposed that the NMRP system leads to crosslink densities that approach those of classical Flory-Stockmeyer theory at the gelation point. The primary reason for this is that the TEMPO controller can inhibit the formation of intramolecular crosslinks and cyclization, which is normal in conventional free radical copolymerization of STY/DVB. Thus, a looser network is produced and the gelation point in relation to

monomer conversion is delayed. The experimental data from Ide and Fukuda (4, 5) also indicated that increasing the amount of DVBP above 1% caused an acceleration after ca 40% conversion. That behavior is similar but less pronounced to that seen in conventional free radical polymerizations, perhaps indicating a diffusional effect in the CRP system caused by higher solution viscosities.

The purpose of our study was to obtain data to check these findings for STY/DVB copolymerizations. Polymerizations were carried out with three levels of DVB: 1, 1.5 and 3% on a mass basis (runs 4, 6 and 7 of Table 1). The conversion vs. time profiles for these runs are presented in Figure 8.

It can be seen in Figure 8 that the addition of DVB, in the rather small amount used in this study, does not have a large effect on the overall rate of polymerization, although the rates of reaction with added DVB are slightly faster than the rates seen with no DVB. This is somewhat different from the behavior seen in conventional free radical copolymerization of STY with DVB where the gel effect becomes more pronounced as the concentration of DVB goes up and an obvious acceleration, enhanced by the diffusional constraint imposed by the early production of a polymer network, is observed (see Figures 1 to 3). It is interesting to note in Figure 8 that the polymerization rate of the system with the highest DVB content (3 wt%, open squares), which would be expected to be the highest, lies between the values of polymerization rate for the systems with 1 wt% and 1.5 wt% of DVB during the pre-gelation period (conversion range lower than 50%), and then the expected behavior (polymerization rate of the system with 3 wt% of DVB being the fastest) is obtained during the post-gelation period, but no strong increase on polymerization rate is noticed in any of the three cases analyzed with DVB. The insert plot in Figure 8 shows exactly the same results, but the results up
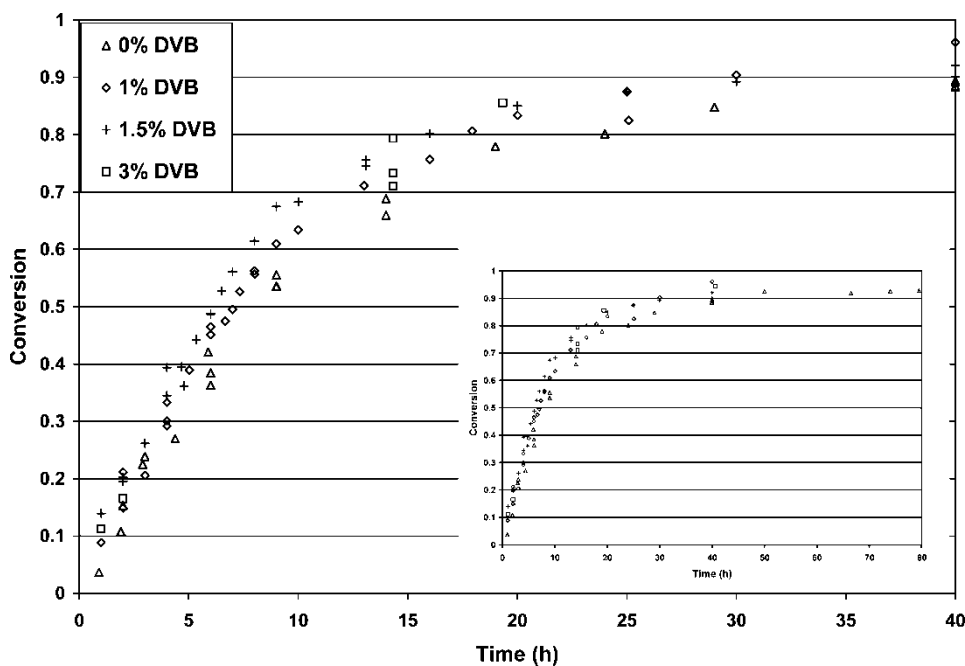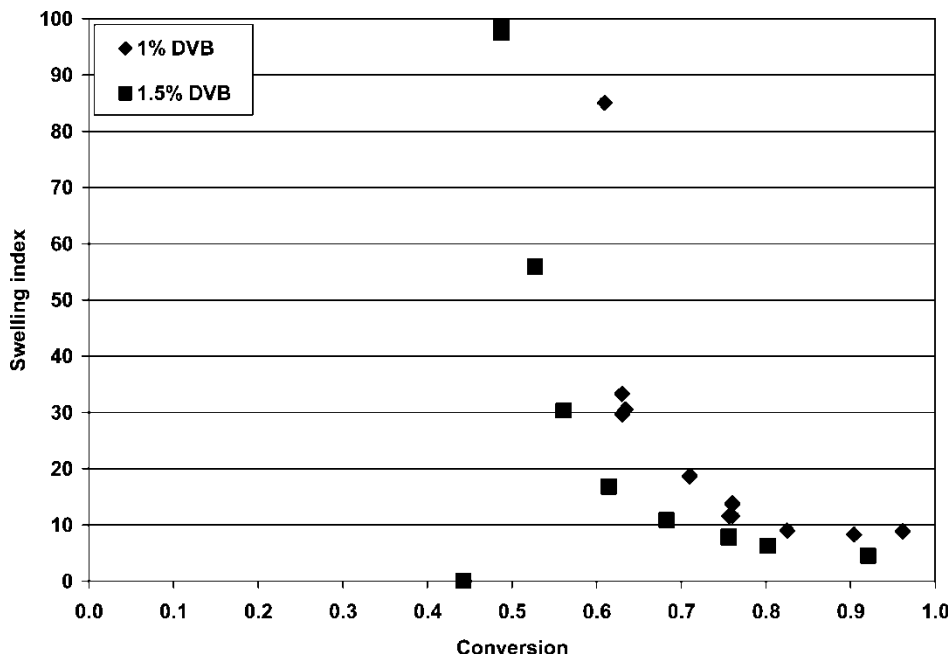

Figure 8. STY/DVB Copolymerization with [BPO] = 0.0355 M, [TEMPO] = 0.0396 M, T = 120°C, and different levels of DVB, as indicated in the legend of the plot.

to 80 h for the case without DVB are shown in the small plot, just to show that no apparent increase on polymerization rate is observed in the long run. This behavior differs from that reported by Ide and Fukuda (4, 5). In their study of STY/DVBP copolymerization, they reported that there was a noticeable acceleration in rate for feeds with 1.5% DVBP after about 40% conversion. This apparent discrepancy may stem from the method they used for assessing the conversion of monomers. In the initial phase of polymerization, conversion was determined by GPC and in the later stages, it was measured by comparing the mass of crude reaction mixture with that of the residue after vacuum drying. It has been repeatedly observed in our labs that complete vacuum drying of polymer (even if not crosslinked) is difficult (e.g., drying to remove low boiling petroleum ether from STY/ Methyl Methacrylate (MMA) polymer (75% STY) could not be achieved in a vacuum oven at 80°C after 1 week). It is likely that it would be more difficult to dry crosslinked products completely because of entrapment of monomer in the matrix. Given that the product of the Fukuda study (4, 5) was crosslinked, drying of STY from the matrix would be extremely difficult, especially since the STY monomer has a high affinity for the copolymer. Such possibilities would lead to higher conversions for a given sample, and thus affect the observed kinetic trends. This may explain the apparent acceleration observed in the kinetic data presented by Ide and Fukuda (4, 5).

Gel content in toluene was measured for samples from runs with 1 and 1.5% DVB. These are illustrated in Figure 9. Similarly, the swelling indices were obtained and are shown in Figure 10. The expected behavior of the gel content increasing very rapidly after the gelation point and the swelling index decreasing from a maximum at the gelation point to a plateau lower value at high conversions was obtained. The decrease in the swelling index suggests that the polymer network is loose at the onset
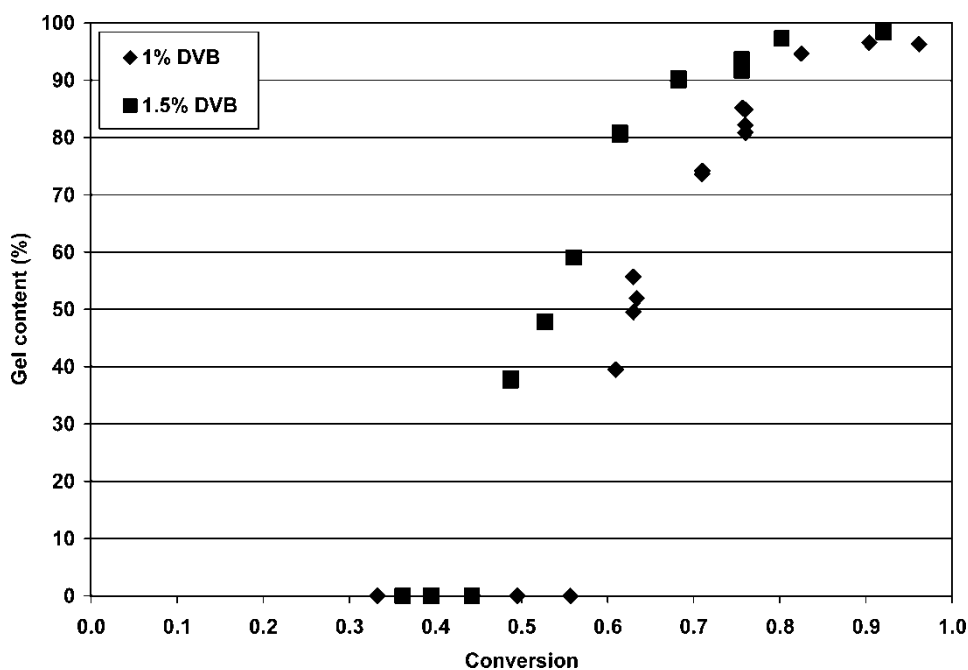
Figure 9. Gel content values with respect to monomer conversion for STY/DVB copolymerization initiated with TEMPO/BPO at 120°C. Effect of DVB level (mass %).

Figure 10. Swelling index values with respect to monomer conversion for STY/DVB copolymerization initiated with TEMPO/BPO at 120°C. Effect of DVB level (mass %).

of the gelation point (low crosslink density), and it becomes compact (much higher crosslink density) as the polymerization proceeds. However, these measurements do not provide precise information on the degree of homogeneity of the obtained polymer network.

Compared to the copolymerization of STY/DVB using conventional free radical polymerization, the NMRP reaction is remarkable for the fact that the gelation point is significantly shifted from about 7 to 50% monomer conversion (compare Figures 3 and 9). This relates to the manner of molecular weight buildup in NMRP where the initial chain lengths are small and, therefore give a reduced probability of crosslinks in the initial phase of reaction.

The trends in molecular weight development were also examined with respect to monomer conversion levels. The results obtained for the runs with 1 and 1.5 wt% DVB are shown in Figure 11. It can be seen that at the start of the polymerization the molecular weights are low, as seen with NMRP homopolymerization of styrene. The data show an obvious discontinuity as the point from a conversion of 8% shows higher molecular weight values (of both M_n and M_w) than those at 20–40% monomer conversion. Given the general trends seen in this experiment, and in other runs using NMRP, this point looks like an outlier. It can be seen from the figure that the number average molecular weight shows a steady increase with conversion, as in nitroxide mediated radical homopolymerization of styrene. In contrast, the weight average molecular weight of the samples increases abruptly with conversion, prior to the gelation point, as shown in Figure 11. This behavior, characteristic of a gelling system, is more clearly observed in Figure 12. The highest PDI comes just before the gelation point, at about 50% monomer conversion. It can be seen from Figures 11 and 12
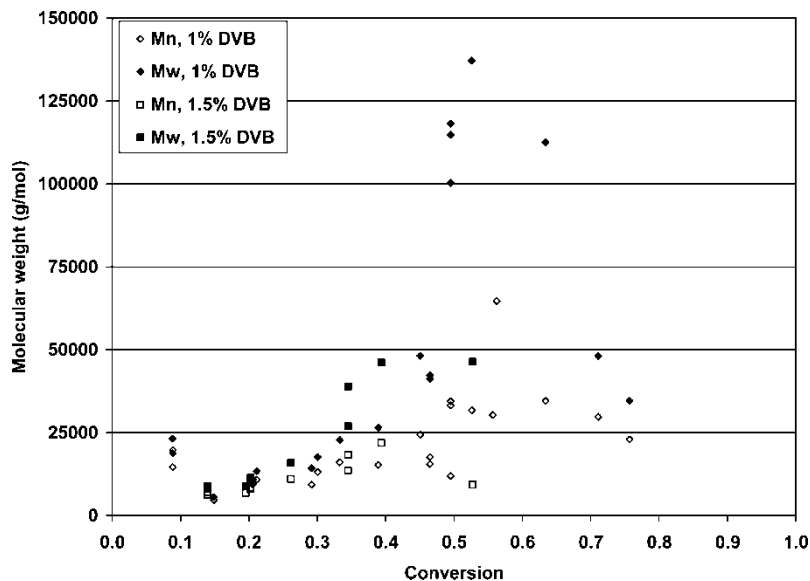
Figure 11. Molecular weight development (M_n and M_w vs. conversion) for nitroxide-mediated radical copolymerization of STY/DVB (DVB = 1 and 1.5 wt%).

that after the gelation point is reached, there is a drop in the weight average molecular weight (observed also as a decrease on PDI in Figure 12). This is because only the soluble fraction of the produced material is being analyzed and typically this will be lower molecular weight material.
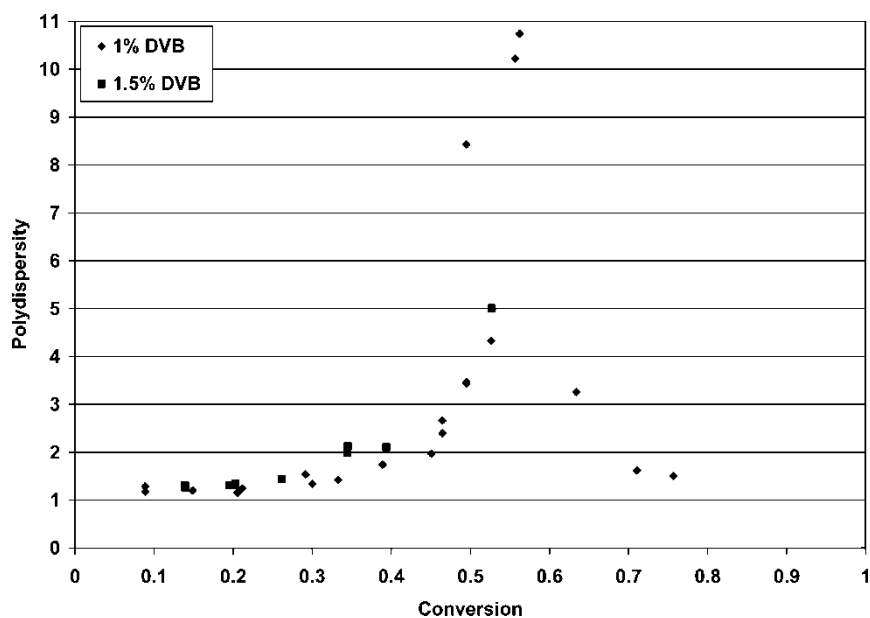
Figure 12. PDI with respect to conversion for nitroxide-mediated radical copolymerization of STY/ DVB (DVB = 1 and 1.5 wt%).

Conclusions

Although, the regular radical copolymerization of STY/DVB has been studied previously in detail, this study is the first to contemplate the copolymerization of such monomers at high temperatures (120°C). Our study of styrene/DVB copolymerization in the presence of TEMPO and BPO considers a different crosslinker, a different type of NMRP process (bimolecular instead of monomolecular), and provides more experimental data than the previous reports from Ide and Fukuda (4, 5). These kinetic studies will be very useful for future model validation studies from ours and other groups.

The maximum conversion reached in the NMRP of styrene was 91%. The addition of small amounts of crosslinker, aimed at increasing the molecular weight of the polymer without completely losing the living behavior of the system, so that DC effects could be evident even if conversions were not too high, was not successful. Although a polymer network was produced, with its corresponding divergence in PDI at the gelation point, the increase on PDI occurred only at the close vicinity of the gelation point, changing from PDI values significantly lower than 2 to infinite PDIs at the gelation point in rather short times. Nevertheless, the importance of DC effects cannot be disregarded without carrying out further experiments and modeling studies.

Our experimental results on the kinetics of polymer network formation in the presence of a nitroxide controller coincide with previous studies in the sense that adding a CRP controller delays the gelation point. Some of our results (PDI vs. conversion profile diverging very rapidly from PDI values lower than 2, and swelling index promptly reaching a steady value) suggest that the produced polymer networks are more homogeneous than those obtained by conventional copolymerization of vinyl/divinyl monomers, but more experiments, focused on obtaining a more direct measure of the crosslink density distribution of the polymer network, should be carried out.

Acknowledgements

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