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Polymerization conditions for the bimolecular NMRP of styrene using TEMPO and BPO were revisited and expanded with the objective of creating a more complete and reliable source of experimental data for parameter estimation and model validation purposes. Three different experimental techniques were assessed for the NMRP of styrene. The reliability of results produced in vials with inert nitrogen atmosphere was evaluated, taking as reference the more reliable technique using sealed ampoules with inert atmosphere. Polymerization rate data obtained in vials could be considered reliable if monomer loss was taken into account, but the reliability of molecular weight data at high conversions may be questionable. Polymerizations at 120 and 130°C and with TEMPO to BPO, molar ratios of 0.9 to 1.5 were carried out. Comparison of the experimental data collected against predictions obtained with a detailed kinetic model previously reported in the literature suggest that either the present understanding of the reaction system is incomplete, or some of the kinetic rate constants reported in the literature are not accurate, or both. Guidelines on how to address and design future experimental and modeling studies are offered.

Keywords: controlled/living radical polymerization; nitroxide mediated radical polymerization; polystyrene; TEMPO

1 Introduction

Many cutting-edge scientific developments in areas such as aeronautics, biomaterials, nanotechnology and information technology rely on the development of polymeric materials with very specific molecular architectures. These materials can be produced through ionic polymerization processes, which are quite expensive, compared to typical free-radical polymerization technology. Free-radical polymerization processes are more versatile with regard to the types of monomers that can be polymerized and much less expensive. It would be very attractive and profitable to be able to produce materials with sophisticated structures and architectures using free-radical polymerization technology. Partly for these reasons "controlled/'living' radical polymerization" (CLRP) processes have become a major research area in polymer science and engineering.

The area of CLRP has received much attention in the literature in the last fifteen years or so. The topic has been reviewed by Matyjaszewski and Davis (1). Most research groups in polymer science and engineering have focused their research efforts about CLRP on issues such as: the development and lab scale testing of new chemical controllers, the proposal of likely reaction mechanisms and their experimental confirmation or refutal, synthesis of commodity polymers with narrow molecular weight distributions, synthesis of block copolymers, and attempts to design and synthesize polymer molecules with more complex structures. Sound kinetic studies for experimental determination of reliable kinetic rate constants are rare, and usually carried out in non-systematic ways (with some exceptions).

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In this paper we will address the CLRP process known as nitroxide mediated radical polymerization (NMRP). Some of the disadvantages of NMRP include the fact that the first controllers were only good for styrenic monomers, and very low polymerization rates were obtained. The range of controllers has been summarized previously (1, 2). In addition, other controllers have been developed by CIBA (3). The work reviewed illustrates the intensive research aimed at producing more effective controllers for NMRP of monomers besides styrene, and for faster polymerization rates with styrenic ones. Recently, it has been reported that block copolymers synthesized by NMRP are finding their first industrial use as dispersants in the area of pigments, providing unique rheology of pigment concentrates and improved pigment stabilization (4).

In this work, our attention has concentrated on the first experimental system reported by the group of Georges (5–7), namely, the bimolecular NMRP of styrene using 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as controller, and dibenzoyl peroxide (BPO) as initiator. The objective was to generate a source of reliable experimental data for validation of mathematical models of NMRP of styrene which are indeed useful for better understanding of this process, and for providing tools for future optimization studies. These experimental data were intended to cover the full conversion range, and include two different temperatures, and different controller to initiator molar ratios. The performance for NMRP of three common polymerization methods was compared, and cross validation of results between two labs was carried out. The results were analyzed and interpreted using the mathematical model for NMRP of styrene developed by Bonilla et al. (8).

2 Experimental

2.1 Reagents and Purification Methods

Styrene (Aldrich Chemical Co. Inc. 99% S4972-4L), was washed, dried and distilled using standard purification methods (9). TEMPO (Aldrich Chemical Co. Inc., 99%, sublimed, 42,636-9-5G, 2564-83-2) was used as received. However, its purity was checked by measuring the effective concentration of aminoxyl (nitroxyl) free radicals in toluene solution in a Bruker ELEXSYS 500 electro spin resonance (ESR) spectrometer. A solution of a known amount of TEMPO in toluene was placed into the ESR, which had been previously calibrated with a standard of a nitroxyl compound of known concentration. The agreement between the prepared TEMPO concentration and the one placed into the ESR equipment was very good, with only a 1.7 wt% difference.

Dibenzoyl peroxide (BPO) came from two different sources, and it was used in three different ways. In the preliminary experiments carried out in Lab 1 by Experimenter 1 (see Table 1), BPO from AKZO (PXIW75, 75% BPO and 25% water) was used as received, just taking into account its purity to measure the correct amount, given the corresponding recipe. This BPO is identified as BPO-d in Table 1. For the experiments carried out in Lab 2 by Experimenters 2, 1, 4, and 5, a BPO of higher purity was used (97% Sigma-Aldrich 17,998-1, 94-36-0). This high purity BPO is identified as BPO-p in Table 1. Finally, for the remaining experiments carried out in Lab 1 by Experimenters 1 and 3, the AKZO BPO (BPO-d) was recrystallized from methanol three times. To do so, 40 mL of methanol were poured onto 1 g of BPO in a beaker, carefully dissolving the BPO with heating, and ensuring that the temperature remained below 50°C. BPO was then recrystallized by immersing the beaker in an ice bath. The excess methanol was decanted, and the BPO crystals were dried in a vacuum oven at room temperature until constant weight

Table 1. Summary of polymerization conditions

Run	[BPO], M	[TEMPO]/[BPO]	T (°C)	Remarks
1	0.036	1.1	120	Schlenk tube, Experimenter 1, Lab 1, using BPO-d
2	0.036	1.1	120	20 mL vials, Experimenter 1, Lab 1, BPO-d
3	0.036	1.1	120	20 mL vials, BPO-d, increasing N_2 purge time to 30 minutes, Lab 1, Experimenter 1
4	0.036	1.1	120	5 mm internal diameter (I.D.) ampoules, Experimenter 1, Lab 1, BPO-d
5	0.036	1.1	120	5 mm I.D. ampoules, Experimenter 2, Lab 2, BPO-p
6	0.036	1.1	120	Repeat of run 5, Experimenter 1, Lab 2
7	0.036	1.1	130	5 mm I.D. ampoules, BPO-p, Experimenter 1, Lab 2
8	0.036	1.1	120	5 mm I.D. ampoules, Experimenter 1, Lab 1, BPO-r
9	0.036	1.1	120	20 mL vials, 3 repeats, Experimenters 1 and 3, Lab 1, BPO-r
10	0.036	1.3	130	5 mm I.D. ampoules, BPO-p, Experimenter 4, Lab 2
11	0.036	1.5	120	5 mm I.D. ampoules, BPO-p, Experimenter 4, Lab 2
12	0.036	0.9	120	5 mm I.D. ampoules, BPO-p, Experimenter 4, Lab 2
13	0.036	1.2	120	5 mm I.D. ampoules, BPO-p, Experimenter 5, Lab 2
14	0.036	1.1	130	5 mm I.D. ampoules, BPO-p, Experimenter 4, Lab 2
15	0.036	0.9	130	5 mm I.D. ampoules, BPO-p, Experimenter 4, Lab 2

(approximately 3 days). The procedure was repeated twice more. This three-times-recrystallized BPO is identified as BPO-r in Table 1.

The other chemicals, methanol (Baker, 99.9%); dichloromethane (Baker); sodium hydroxide, 98%, Aldrich; hydroquinone (Aldrich HI790-2, 99%); and tetrahydrofuran (THF), HPLC grade, Baker, were used without further purification.

2.2 *Polymerization Methods*

2.2.1. Polymerization in Schlenk Tube

10 mL of the solution mixture of Styrene, BPO-d and TEMPO were added to a 50 mL Schlenk tube. Argon was bubbled for one hour to remove air. Afterwards, the tube was immersed in a silicone oil bath. The bath was heated with a hot plate stirrer to 120°C. The reaction was allowed to proceed for 40 h, taking samples every hour with a syringe. Each sample was placed on an aluminum dish and weighed immediately after adding 0.02 ml of a 1 wt% hydroquinone solution in THF. The samples were dried in a vacuum oven at room temperature until constant weight was obtained.

2.2.2. Polymerization in Ampoules

Solutions were prepared with the appropriate amounts of TEMPO, BPO and styrene, according to the recipes described in Table 1. Aliquots of the solution were then transferred into the ampoules (5 mm inner diameter). The contents of the ampoules were degassed by three successive freeze-thaw cycles under vacuum (0.03 mbar). The ampoules were torch-sealed under vacuum, and then placed in liquid nitrogen until used. The polymerizations were carried out in a Neslab circulator bath, containing silicone oil, with temperature control, at the predetermined temperature (120 or 130 ±0.1°C). Further details about the procedure to recover the polymer product from the ampoules have been documented before (9).

2.2.3. Polymerization in Vials

A solution of styrene, BPO and TEMPO at the conditions specified for a given run (see Table 1) was prepared. 2 mL of solution was placed in each vial. The vials were capped with Teflon/silicone septa, using a hand crimper (vial capping device), and then placed in an ice bath to reduce levels of evaporated monomer while nitrogen was bubbled for 3 min to remove air from the vials. Once air was removed, the vials were immersed in a PolyScience 4 liter programmable bath circulator with temperature control, at the set temperature of 120 ±0.1°C. The vials were removed from the bath circulator at the planned sampling times and then placed in a bath with ice and salt. The vials were opened and 0.3 mL of a hydroquinone in THF solution (1%) was added to completely stop the reaction. The contents were dissolved in dichloromethane and later precipitated with methanol. The excess solvent was evaporated at 35°C in a vacuum oven. The samples were dried in the vacuum oven until constant weight was obtained.

It is worth mentioning that in the first experiments in vials (runs 2 and 3) the nitrogen flow through the capped vials was left to run for 5 mi, and the vials were not placed in an ice bath during the purge with nitrogen, so that a significant amount of styrene was lost during this procedure. Furthermore, the hand crimper was not well adjusted, so that the caps did not seal properly. Also, instead of dichloromethane, toluene was used as the solvent for the polymer in these runs. The experiments for run 9 (3 repeats with frequent sampling over the full conversion range) were carried out with the improved procedure.

Monomer conversion was measured gravimetrically in the three polymerization techniques. In the case of vials, conversion was referred to the final mass (some monomer was lost by evaporation, despite the fact that the vials were sealed with the caps), instead of the initial mass of monomer fed to the vials.

2.3 *Polymer Characterization*

Number average molecular weight and polydispersity were obtained by size exclusion chromatography (SEC/GPC). Two different set ups were used in different labs. What will be referred to as “GPC 1” was a Waters 150C ALC/GPC with a refractive index detector, equipped with an online degasser. Calibration was carried out using polystyrene standards. Equipment “GPC 2” consisted of an isocratic Waters 515 HPLC pump, a “Waters 717 plus” injector, 3 Waters HR 5E columns, and a Viscotek TDA 302 set of four detectors: refractive index (RI), ultra-violet (UV), low angle laser light scattering (LALLS) and right angle laser light scattering (RALLS), as well as an intrinsic viscosity detector (IV-DP viscometer differential pressure).

3 Results and Discussion

3.1 *Experimental Strategy and Modeling Aspects*

All the conditions addressed experimentally and modeled in this paper are summarized in Table 1. Since the main purpose of this study was to generate experimental data which could be used for model validation purposes, it was of great importance to make sure that the experimental data obtained were reliable. Part of the validation procedure included making certain that the experimental data were reproducible if obtained by different operators of the same lab, and personnel from different labs. Another important aspect was to cross-validate data using different GPC equipment for molecular weight measurements. Once we were certain about the reliability of the experimental data, it was important to run experiments over a wide range of operating conditions, which included: the full conversion range, at least two different temperatures, and several [TEMPO]/[BPO] molar ratios.

One of the most accurate methods to obtain precise kinetic data in polymerization processes is to perform ampoule polymerizations in as thin as possible ampoules. However, for various reasons, not all labs can be adequately equipped to carry out this type of polymerization. In addition, sometimes there is a need to make larger polymer samples that are not feasible by ampoule methods, so polymerizations in large volume flasks (10 to about 100 ml flasks) or glass vials (in the order of 2 to about 50 ml of reaction volume) are common in academic and industrial labs. In the case of conventional radical polymerization, polymerization in vials or large flasks may not be adequate for kinetic studies, due to non isothermal conditions across the reacting system, with temperature differences between the center line and the wall in contact with the heating/cooling fluid between 5 to 70°C (10).

As mentioned before, the experiments reported in this paper were carried out using three polymerization techniques (polymerizations in a Schlenk tube, vials and ampoules) in two labs (labeled as Labs 1 and 2 in Table 1) by 5 experimenters (Experimenters 1 to 5), using two different GPCs (GPCs 1 and 2). This unique blend allowed us to carry out a cross-validation study, taking into consideration several sources of variation in the reliability of the obtained results. Once reliable results were being produced, the effects of temperature and [TEMPO] to [BPO] molar ratio on monomer conversion and molecular weight development were experimentally addressed.

Model simulations were produced for all the cases described in Table 1, and were used to analyze the results. The polymerization mechanism and kinetic model used in this paper are the same as those proposed by Bonilla et al. (8). The kinetic rate constants were either estimated by Belicanta Ximenes et al. (11), or taken from Zhang and Ray (12). All the kinetic rate constants used in the calculations are listed in Table 2.

The model equations were solved with a self developed Fortran code (11). The Predici® commercial software was also used to simulate the different polymerization conditions studied in the paper. The profiles produced with our Fortran code overlapped with the profiles produced with Predici® in most of the cases analyzed in this paper.

3.2 Comparison of Polymerization Methods

Figure 1 shows a comparison of conversion versus time experimental data obtained by the three polymerization methods for NMRP of styrene at 120°C and [TEMPO]/[BPO] = 1.1. The experimental data corresponding to run 5 were obtained by Experimenter 2, in Lab 2 (13). These data points were taken as reference, not only because of the experience level of the personnel, but also due to the fact that a highly pure BPO (BPO-p) was used. Repeats of the experiments in ampoules by Experimenter 1 in Lab 2 (run 6) and Experimenter 1 in Lab 1 (run 8) were carried out to verify the reproducibility and reliability of the ampoule polymerization technique. The agreement between the three independent replicates of the ampoule polymerization technique was very good.

The experimental data of run 1 were obtained from a Schlenk tube experiment, using BPO-d, in Lab 1. It is observed in Figure 1 that faster polymerization rates relative to the reference set were obtained at intermediate and high conversions. This may be related to the sampling method (taking out a sample with a syringe, or a spatula, if the viscosity was very high), and probably poor mixing

Table 2. Kinetic parameters used in the model

Parameter	Units	Value or function	Reference
k_d(BPO)	s^{-1}	$1.7 \times 10^{15} \exp(-30000/RT)$	(12)
f_0		0.54–0.55[a]	(12)
k_{dim}	$L\ mol^{-1}\ s^{-1}$	$188.97 \exp(-16185.1/RT)$; (3×10^{-8}, @120°C)[b]	(11, 18)
k_{ia}	$L\ mol^{-1}\ s^{-1}$	$6.359 \times 10^{12} \exp(-36598.55/RT)$ (1.2×10^{-10}, @120°C)[b]	(11, 19)
k_{p0}	$L\ mol^{-1}\ s^{-1}$	$4.266 \times 10^{7} \exp(-7769.17/RT)$	(12)
k_{t0}	$L\ mol^{-1}\ s^{-1}$	$2.002 \times 10^{10} \exp(-3081.84/RT)$	(12)
k_{td}/k_{t0}		0.0	(11)
k_{fM}	$L\ mol^{-1}\ s^{-1}$	$9.376 \times 10^{6} \exp(-13372/RT)$	(12)
k_{fD}	$L\ mol^{-1}\ s^{-1}$	0.0	Neglected
k_{a2}	s^{-1}	0.0	(11)
k_{d2}	$L\ mol^{-1}\ s^{-1}$	0.0	(11)
k_{da}	$L\ mol^{-1}\ s^{-1}$	$5.03 \times 10^{9} \exp(-3722/RT)$; ($8 \times 10^{7}$, @120°C)[b]	(12, 18)
k_a	s^{-1}	$2.0 \times 10^{13} \exp(-29683/RT)$; ($8 \times 10^{-4}$, @120°C)[b]	(12, 18)
k_{decomp}	s^{-1}	$5.7 \times 10^{14} \exp(-36639.6/RT)$	(12)
k_{h3}	$L\ mol^{-1}\ s^{-1}$	0.001 (@ 120°C), 0.01 (@ 130°C)	(8, 11)

[a] Initiator efficiency (f) range depending on the reaction temperature.

[b] Values used to generate the "alternate profile" of Figure 1.

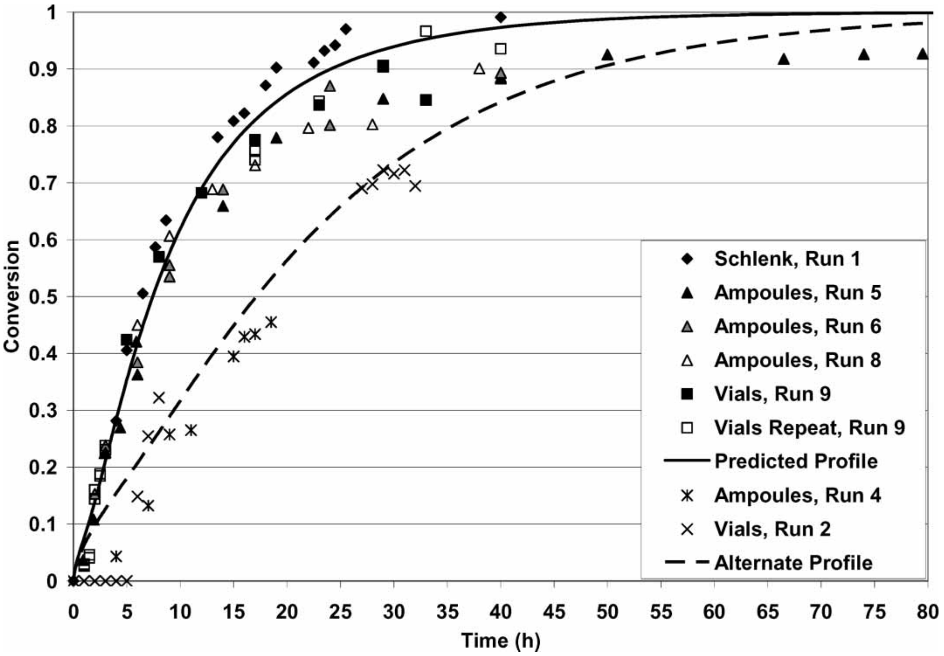

Fig. 1. Comparison of experimental data and model predictions of conversion vs. time, at 120°C and [TEMPO]/[BPO] = 1.1, using three polymerization techniques.

inside the relatively wide tube, at high conversions (large viscosities).

As mentioned in the experimental section of this paper, the polymerization technique using vials was improved for run 9, based on the analysis of results from runs 2 and 3 (run 3 not shown in Figures 1 to 3, but reported in Roa-Luna (14)). Monomer loss during the nitrogen purge and polymerization stages in the best polymerization conditions of run 9 (labeled as V3 in Figures 2 and 3) was less than 5 wt% up to a 70% monomer conversion, but it could be as high as 30 wt% (monomer loss) in the region of 80–90% monomer conversion (compared to about 50% loss in the preliminary

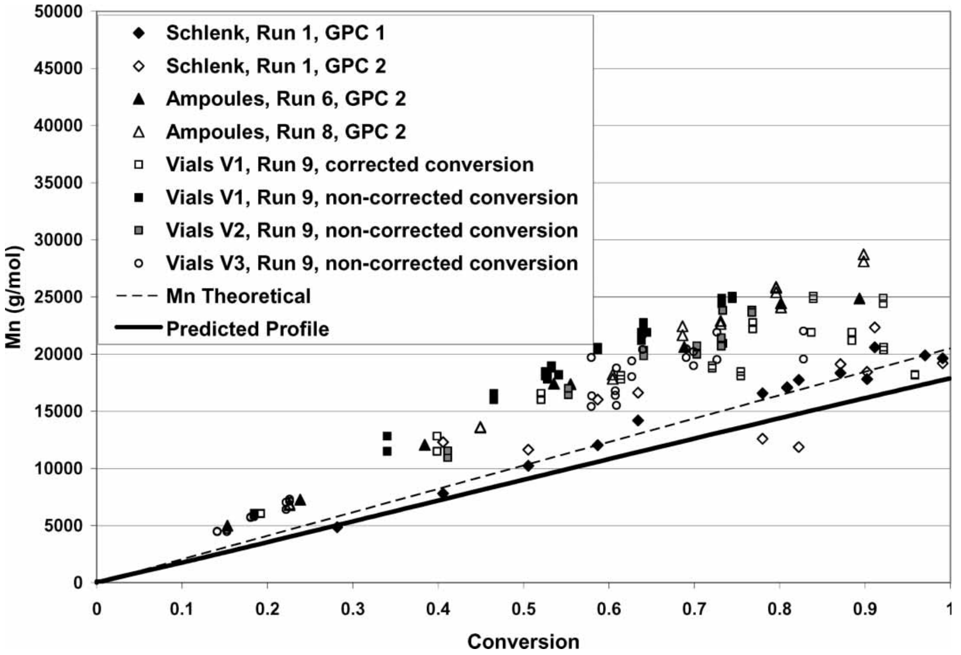

Fig. 2. Comparison of experimental data and model predictions of M_n vs. conversion, at 120°C and [TEMPO]/[BPO] = 1.1, using three polymerization techniques.

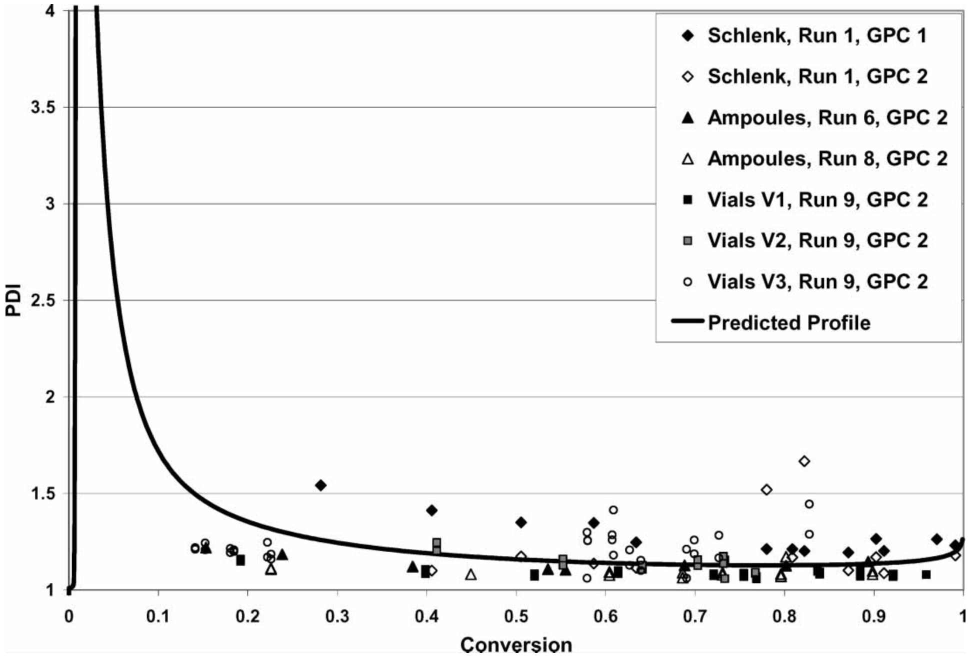

Fig. 3. Comparison of experimental data and model predictions of PDI vs. conversion, at 120°C and [TEMPO]/[BPO] = 1.1, using three polymerization techniques.

experiments (14)). If monomer conversion was calculated based on the final mass of contents in the vial (as done for run 9), and not on the initial monomer mass (as in runs 2 and 3), the agreement between the ampoule and the vials experimental data was very good, even if a significant amount of monomer was lost during polymerization. This can be seen in Figure 1, where the ampoule data (runs 5, 6 and 8) and the vials data (run 9 and its repeat) show very good agreement.

The agreement between the model predictions obtained with our implementation of the Bonilla et al. model (8) ("predicted profile" in Figure 1) and the experimental data obtained in ampoules was good up to about 50% monomer conversion, but the model overestimates the polymerization rate at high conversions, and the maximum conversion achieved at the polymerization conditions. The model predicts 90% conversion at about 20 h, and total conversion at about 60 h, whereas the experimental data reach 90% monomer conversion at around 40 h, and the conversion does not go beyond 93%. As observed in Figure 1, there seems to be a better agreement between the model predictions and the experimental data obtained in a Schlenk tube (a slight underestimation obtained with the model), and even better between the model and the experimental data in vials (slight overestimation with the model at high conversions).

Figures 2 and 3 show plots of number average molecular weight, M_n, and polydispersity (PDI) versus conversion, respectively, for all the results related to the comparison of polymerization techniques (runs 1 to 6, 8 and 9 of Table 1). The overall scatter in both cases (M_n and PDI) is rather large if the results of the three polymerization techniques are combined, but the scatter is small if the polymerization techniques are considered independently. A linear trend on the M_n versus conversion profile (Figure 2), and PDI values lower than 1.5 in most cases (mostly in the range 1.07 to 1.3) (Figure 3), typical of living polymerization systems, are clearly observed for most data sets. The M_n values for the Schlenk case are the lowest, as expected, since they correspond to the highest polymerization rate. The experimental data obtained in ampoules and vials show the same average values, but the scatter of the experimental data obtained in vials is larger. The experimental values of M_n (Figure 2) and PDI (Figure 3) obtained in vials, using the "corrected conversion", show a large spread (shown as small empty squares) at conversions higher than 50%. The experimental data obtained from ampoule experiments (open and solid triangles) show a smaller experimental error. In Figure 2, the experimental data of M_n obtained in vials are also plotted versus conversion based on initial mass (solid squares), showing a better agreement, but not having values after 75% monomer conversion (because of the monomer lost by evaporation). Therefore, it seems that using polymerization in vials can provide reliable kinetic data for polymerization rate, but not good enough for molecular weight development in NMRP of styrene at high conversions. Also shown in Figure 2 are the theoretical (monomer concentration to initiator concentration at any given time) and model calculated profiles. The model-calculated profile lies below the theoretical one, but both underestimate the actual molecular weights. The lower predicted values of M_n obtained with the mathematical model may be caused by the transfer to monomer reaction in the reaction mechanism being considered in the mathematical model, or possibly to inaccurate estimates of some of the kinetic rate constants involved in the reaction mechanism. The model predicted profile of PDI vs. conversion shown in Figure 3 agrees well with the experimental data, which lie on the average PDI most of the time. The calculated profile predicts high PDIs (higher than 5) at the beginning of the polymerization, decreasing to lower than 2 at about 10% monomer conversion, and remaining fairly constant around 1.1 and 1.2, showing a very slight increase at very high conversions.

It is interesting to note that the best agreement between experimental data and model predictions for polymerization rate (Figure 1), M_n vs. conversion (Figure 2), and PDI vs. conversion (Figure 3), at 120°C and [TEMPO]/[BPO] = 1.1, is obtained with the experimental data from a Schlenk tube (in the case of polymerization rate, the results with vials also showed good agreement). Since it was explained before that the treatment of data from samples obtained by the vials technique might lead to higher than real polymerization rates (with their corresponding lower molecular weights), this result might seem contradictory at first sight. However, the result is expected, if one considers that one of the polymerization methods used by the group of Georges (see for instance, references 15, 16 and 17, since their polymerization method is not described in detail in their first publications), consisting of a round three-necked flask under argon or nitrogen blanket, and withdrawing samples with a pipette (17), is very similar to the polymerization in a Schlenk tube used in run 1 of our experiments. Since the kinetic rate constants for activation and deactivation in NMRP of styrene with TEMPO have been estimated using experimental data generated by the group of Georges, it is then perhaps not surprising that our model predictions agree better with the Schlenk-produced experimental data.

The importance of developing reliable and complete experimental databases for parameter estimation purposes in the study of polymerization processes such as NMRP might be more clearly visualized with the aid of a simple case study. As explained before, our own preliminary experiments in vials and ampoules (runs 2 and 4, respectively) produced low polymerization rates and large scatter of experimental data in the M_n and PDI versus conversion profiles. The reasons for those deviations have been clearly identified (monomer loss not taken into account in the vials experiments, and several minor experimental flaws in the ampoules technique) and documented in detail elsewhere (14). Some of the conversion versus time experimental data obtained in runs 2 and 4 are included in Figure 1 for our case study. It is clearly observed that the polymerization rate is much lower than in the other more reliable cases, but there is some agreement between the two runs (2 and 4). To continue with our case study, a model predicted profile (labeled as "alternate profile" in Figure 1) was obtained using "slightly" different kinetic rate constants, also "taken from the literature" (values in brackets in Table 2). It is observed that the agreement between the "alternate profile" and our erroneous experimental data is quite good. If we were not aware of the errors occurring during runs 2 and 4 (which required a team effort between two research groups to identify and eliminate), we could have argued that the experimental data agree with model simulations using parameters from the literature, and thus use erroneous experimental data (runs 2 and 4) to "validate" other simulation or optimization studies, eventually leading to inaccurate conclusions or process designs.

3.3 *Effect of Temperature*

The primary experimental and simulation results of NMRP of styrene with TEMPO and BPO were based on one set of conditions: 120°C, and using [TEMPO]/[BPO] = 1.1. In Figures 4, 5, and 6 experimental and predicted profiles of conversion vs. time, M_n versus conversion, and PDI versus conversion, respectively, at 130°C and [TEMPO]/[BPO] = 1.1, are shown. In Figure 4, the simulated profile of conversion vs. time at 120°C is also shown, as reference, for comparison purposes. As expected, the polymerization proceeds faster at 130°C than at 120°C. As in the lower temperature case, the agreement between experimental data and the predicted profile is good up to about 70% monomer conversion. From there on, the predicted profile significantly overestimates the polymerization rate. The model predicted and the theoretical profiles of M_n versus conversion lie below the experimental data, although rather closer than at the previous conditions (120°C), as shown in Figure 5. A slight reduction in the values of M_n, with respect to the profile obtained at 120°C, is observed at 130°C (compare Figure 5 against Figure 2), which is the expected effect of temperature on molecular weight in free radical polymerization. In the case of PDI vs. conversion, once again, the model predicts high PDI values in the early stages of the polymerization. However, in this case the tendency towards low PDIs (lower than 1.3) is obtained later in the polymerization, as compared to the case at 120°C. It is also observed that both the experimental and predicted PDIs are slightly higher than the values obtained at 120°C. Also, the agreement between experimental data and the predicted profile of PDI versus conversion is not as good as in the case at 120°C. It is also observed in Figure 6 (and in Figure 3), that PDI seems to increase from about 1.2 to about 1.6 when going from a conversion level of 90 to 100%. The determination of PDI with GPC does not seem to be accurate enough to capture that interesting increase at very high conversions.

3.4 *Effect of [TEMPO]/[BPO] Molar Ratio*

Figure 7 shows the effect of the ratio of TEMPO concentration to BPO concentration ([TEMPO]/[BPO]) on polymerization rate, expressed as conversion versus time, at 120°C. Experimental data and simulated profiles at [TEMPO]/[BPO]

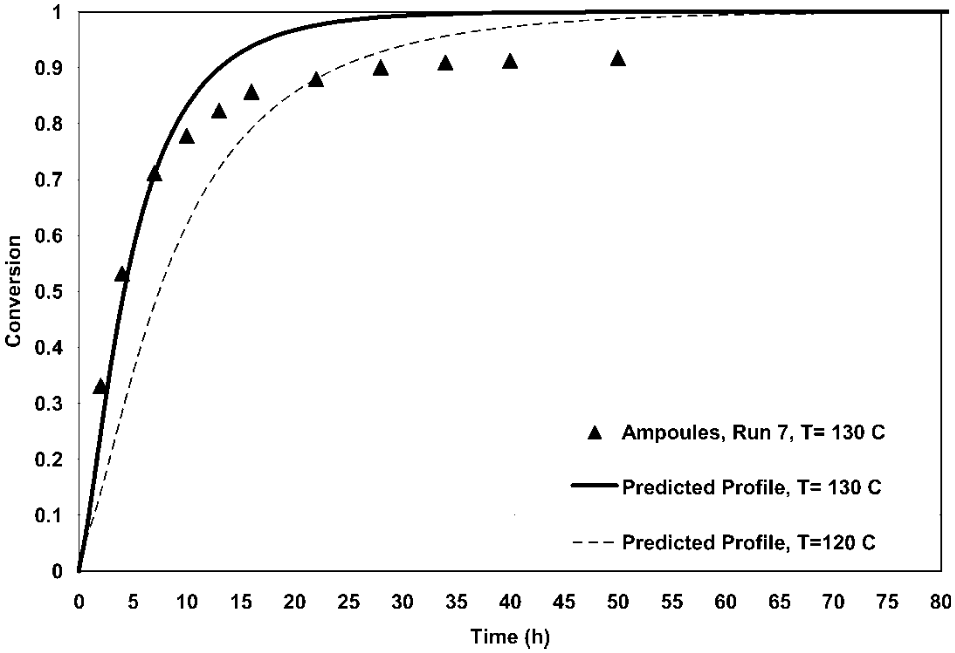

Fig. 4. Comparison of experimental data and model predictions of conversion vs. time at the conditions of run 7.

ratios of 0.9, 1.1, 1.2 and 1.5 are shown in Figure 7. As expected, the larger the ratio (the more TEMPO fed to the recipe), the slower the polymerization will proceed. Both the experimental data and the predicted profiles show that trend. However, the effect is much more pronounced in the experimental data than the predictions of the model. The model predicts a crossover of curves, with the limiting conversion reaching higher values as the [TEMPO]/[BPO] ratio is increased. That crossover of curves is not captured with the experimental data, but that may be explained by the fact that the experimental error seems to be higher than the sensitivity needed in the high conversion region to observe that effect. Another interesting feature of the NMRP polymerization captured with the experimental data at [TEMPO]/[BPO] = 1.5 is the existence of an apparent induction time, related to the time needed to reach an equilibrium between activation and deactivation of polymer radicals, which lasts about 2.5 h at those conditions.

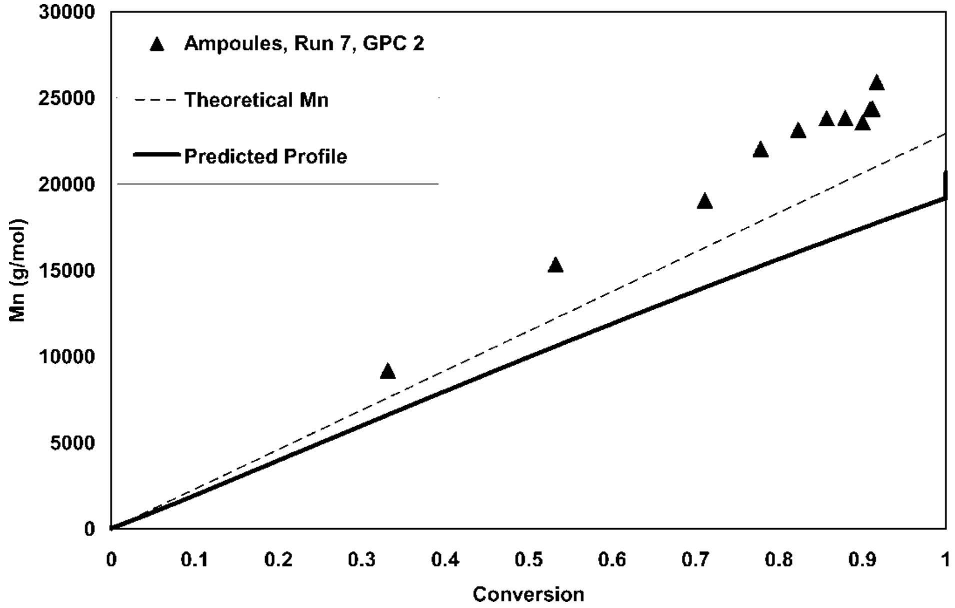

Fig. 5. Comparison of experimental data and model predictions of M_n vs. conversion at the conditions of run 7.

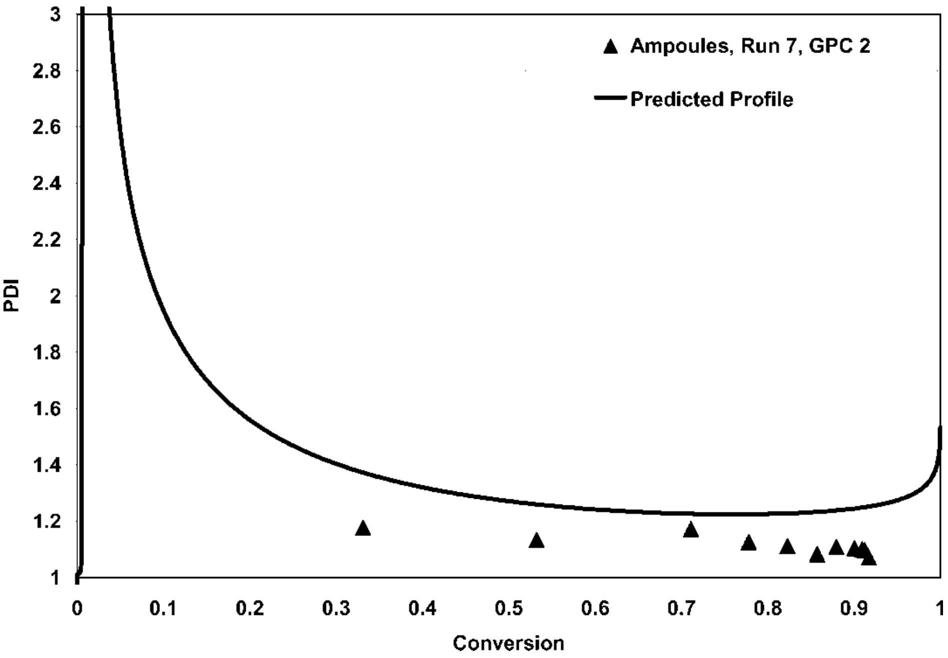

Fig. 6. Comparison of experimental data and model predictions of PDI vs. conversion at the conditions of run 7.

Figure 8 shows the corresponding profiles to Figure 7 for number average molecular weight development. The symbols and lines used correspond to the same [TEMPO]/[BPO] ratios used in Figure 7. It is observed that higher values of the number average molecular weight, M_n, are obtained when the [TEMPO]/[BPO] ratio is decreased, namely, when the polymerization rate is increased. In conventional free radical polymerization M_n decreases due to the increased rate of bimolecular radical termination when temperature increases, which dominates over the increase of propagation rate. In CLRP the effect of bimolecular termination is suppressed to a greater extent, so that increasing temperature promotes the controlled growth of the polymer chains by allowing the chains to grow faster, with the increase in the termination step not being significant. The model captures nicely this behavior, but all the profiles lie

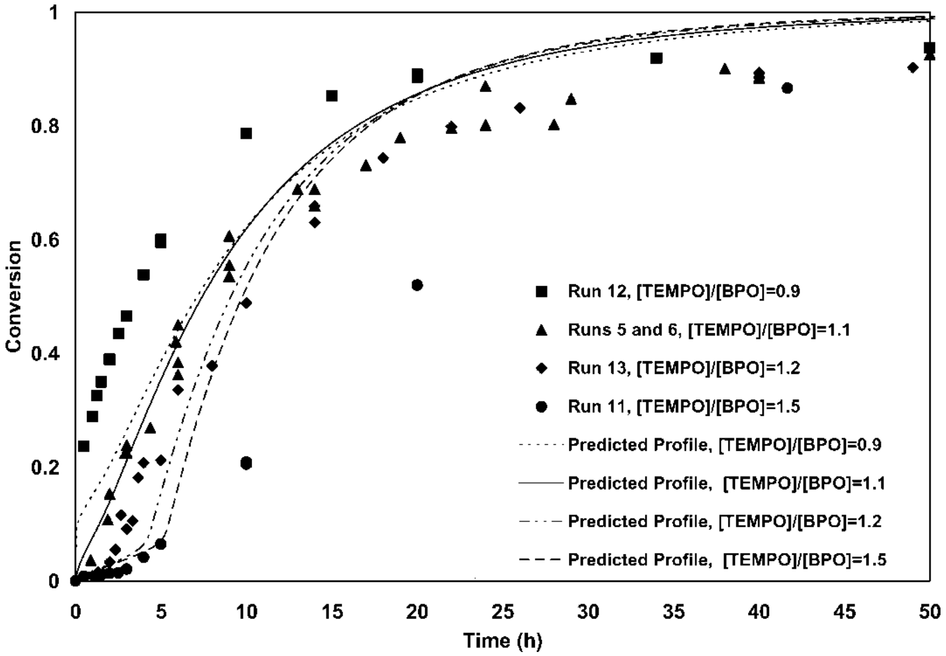

Fig. 7. Effect of [TEMPO]/[BPO] ratio on polymerization rate at 120°C.

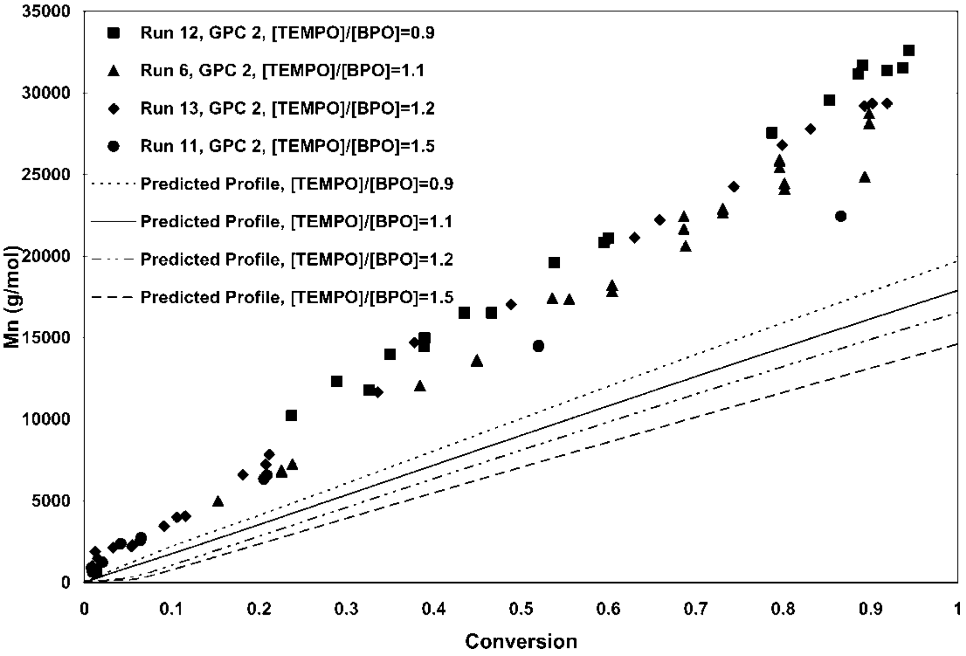

Fig. 8. Effect of [TEMPO]/[BPO] ratio on number average molecular weight, M_n, at 120°C.

much lower than the experimental data, as noted in the previous subsection of this paper.

Figure 9 shows a comparison of model simulations against experimental data of PDI vs. conversion, at 120°C and the same [TEMPO]/[BPO] ratios analyzed in Figures 7 and 8 for polymerization rate and M_n development, respectively. The experimental data at [TEMPO]/[BPO] = 0.9 show that PDI is higher than the corresponding values at the other ratios, at low conversions. At this ratio, it takes up to about 60% monomer conversion to reach the same level in PDI of around 1.2, a value reached much sooner in the other cases. The experimental data of PDI at [TEMPO]/[BPO] ratios of 1.1, 1.2 and 1.5 do not show much difference. Very low values, between 1.07 and 1.2, are obtained for those three

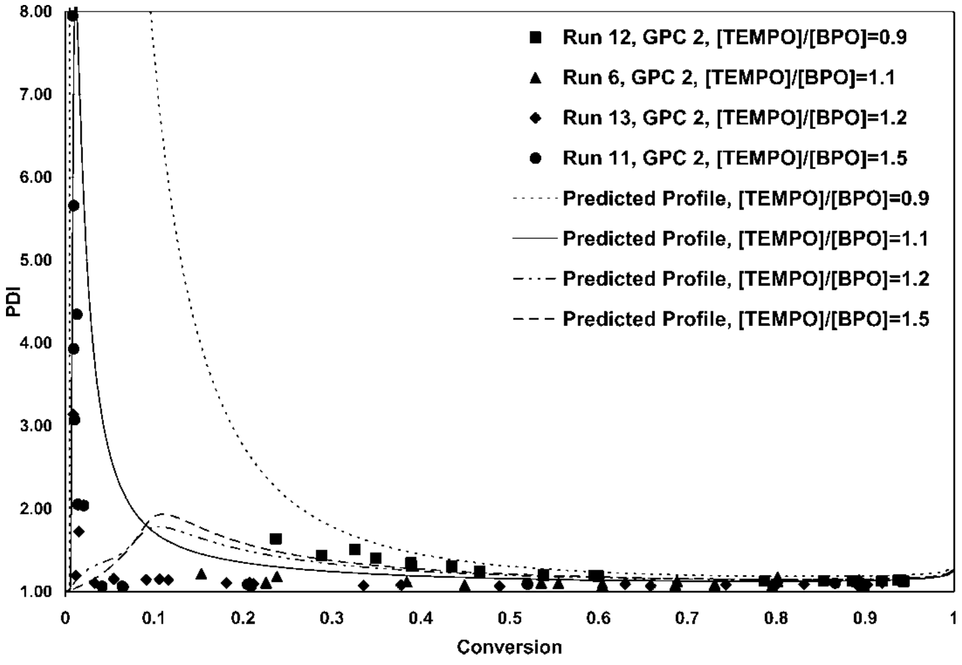

Fig. 9. Effect of [TEMPO]/[BPO] ratio on polydispersity, PDI, at 120°C.

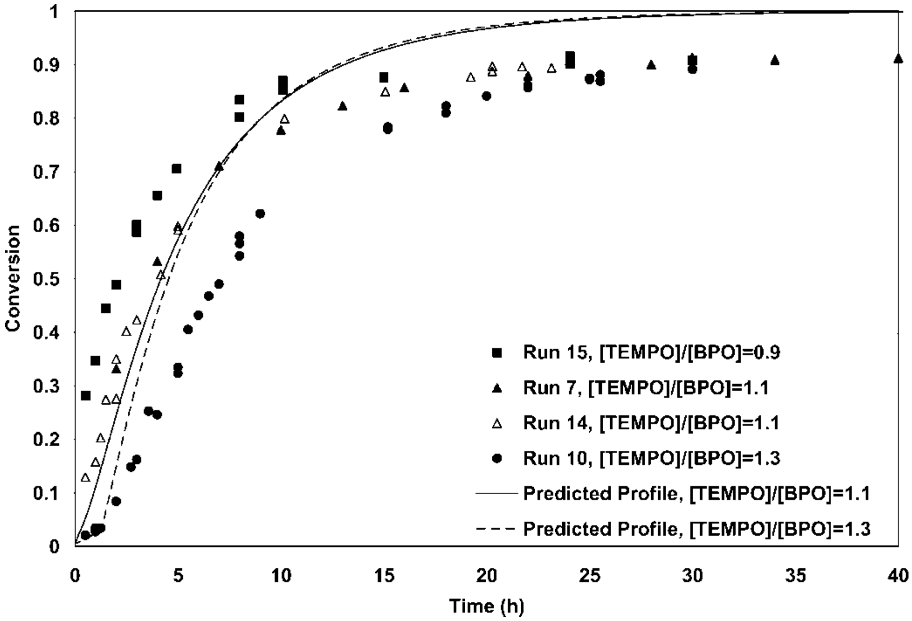

Fig. 10. Effect of [TEMPO]/[BPO] ratio on polymerization rate at 130°C.

ratios, and they appear more as repeats of the same conditions than results from different conditions. That means that a very good control can be achieved with a [TEMPO]/[BPO] = 1.1, which is close to the equimolar case, given the initiator efficiency. The predicted profiles at [TEMPO]/[BPO] = 0.9 and 1.1 show that very high PDIs are predicted at very low conversions, with higher PDIs from the reaction where [TEMPO]/[BPO] = 0.9. The predicted profiles at [TEMPO]/[BPO] = 1.2 and 1.5 show that the maximum on PDI is significantly reduced, but shifted towards higher conversion values, as the ratio increases, although the profile at [TEMPO]/[BPO] = 1.5 shows higher PDIs than the profile at [TEMPO]/[BPO] = 1.2. Many samples were taken during the very low conversion range in the experiments at [TEMPO]/[BPO] = 1.5. It is very interesting to observe that the measured PDIs at that ratio show the trend predicted by the model, namely, that PDIs as large as 8.0 are obtained at very low conversions. However, those measured PDIs at [TEMPO]/[BPO] = 1.5 in the early stages of the polymerization, do not agree with the predicted profile at that ratio, which showed a maximum PDI of 1.93 at a 11% monomer conversion, whereas the experimental maximum of

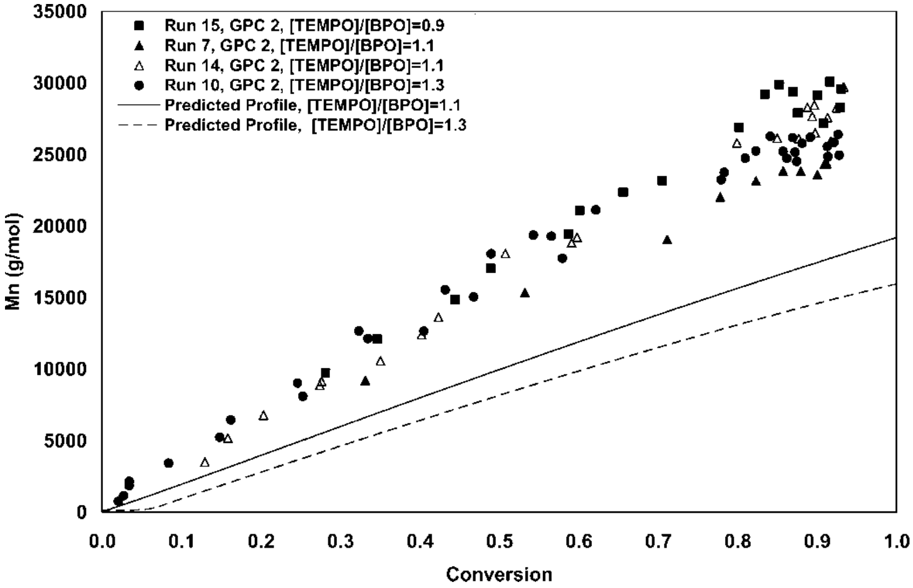

Fig. 11. Effect of [TEMPO]/[BPO] ratio on number average molecular weight, M_n, at 130°C.

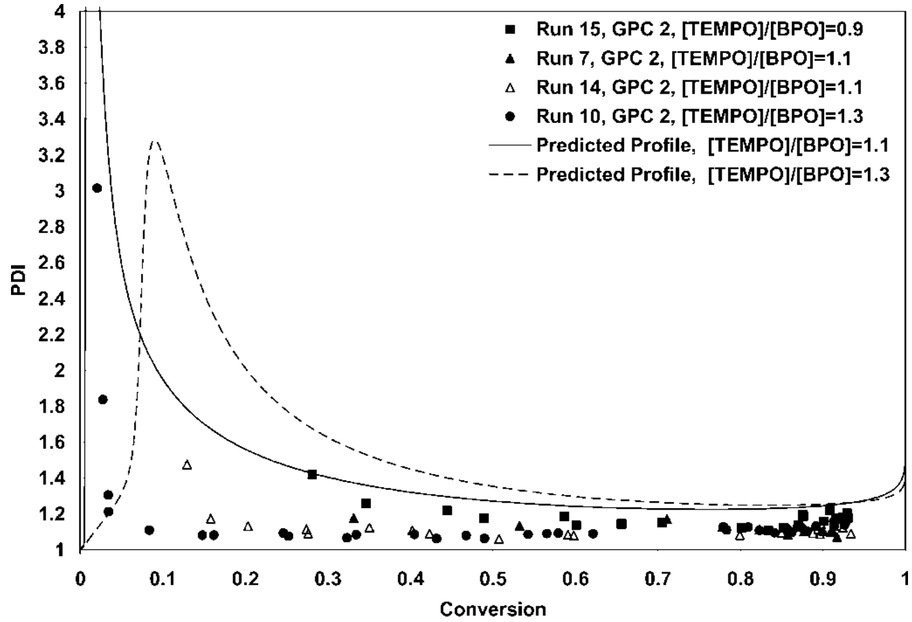

Fig. 12. Effect of [TEMPO]/[BPO] ratio on polydispersity, PDI, at 130°C.

PDI = 7.95 was obtained at 0.8% (less than one percent) monomer conversion.

Finally, Figures 10, 11, and 12, show a comparison of model predictions against experimental data of conversion vs. time, M_n vs. conversion, and PDI vs. conversion, respectively, for the NMRP of styrene, at 130°C, and [TEMPO]/[BPO] = 0.9, 1.1 and 1.3. As in the case at T = 120°C (Figures 7–9), the model predictions show the correct trends, but the quantitative agreement is not good, particularly at the larger [TEMPO]/[BPO] ratio. This again points to the same fact discussed before, that simply some of the kinetic rate constants for NMRP of styrene used in the model calculations (taken from the literature) may not be accurate. In a recent paper from our group we have demonstrated that the agreement between the predicted profiles and some of the experimental data presented in this contribution can be improved by adjusting the parameters related to initiation (initiator efficiency), thermal self-initiation and the so called enhancement reaction (20).

4 Conclusions

A reliable experimental database of polymerization rate and molecular weights (M_n and PDI vs. conversion), at 120 and 130°C and several [TEMPO] to [BPO] ratios, for the NMRP of styrene has been generated. It was suggested that polymerizations in vials may provide reliable kinetic data of polymerization rate versus time, up to high conversions, if monomer losses are accounted for, and conversion is referred to the final total mass. However, the experimental data of M_n and PDI vs. conversion may be inaccurate at conversions higher than 50%. It was also suggested that large flasks with withdrawal of samples from the same flask may not be adequate for accurate kinetic studies of NMRP of styrene at high temperatures (120 to 130°C) and high conversions (larger than 50% monomer conversion).

Overall, the predictions obtained with the model of NMRP of styrene developed by Bonilla et al. (8), overestimate the polymerization rate at high conversions (higher than 70% monomer conversion), underestimate the number average molecular weight, and provide satisfactory predictions of PDI vs. time, at the two temperatures studied here (120 and 130°C). Our experimental data corroborated the model predictions of large PDIs at very low conversions, although the quantitative agreement was not very good in that conversion range. The qualitative effect of [TEMPO]/[BPO] on polymerization rate and molecular weight was adequately reproduced experimentally, but the quantitative agreement is not good.

The adequate qualitative trends predicted by the model and the inaccurate quantitative description of the behavior of the polymerization system suggest that the kinetic rate constants reported in the literature are not reliable enough for predictive purposes. It seems that some of those kinetic rate constants (the ones related to activation and deactivation of polymer radicals) are biased towards higher than real polymerization rates, due to the polymerization techniques behind the experimental data used for parameter estimation studies. The fact that deviations on polymerization rate are obtained at high conversions suggest that diffusion-controlled (DC) effects (DC-termination, DC-propagation, DC-activation and DC-deactivation) may be an issue to consider in future model improvements. It may also be possible that the reaction mechanism is incomplete or imprecise.

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