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Experimental Study of the TEMPO Mediated Copolymerization of Styrene with Divinylbenzene

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Introduction

Since the discovery of controlled radical polymerization (CRP) in the early nineties (Georges et al., 1993), an ever increasing activity has been focused on the production of polymers with narrow molecular weight distributions and well-defined architectures (such as block copolymers, stars or brushes). This work describes an experimental research on the nitroxide-mediated radical polymerization (NMRP) of styrene (S) and divinylbenzenes (DVB) in xylene (X) solution at 130 °C, using the stable radical TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) as mediator and AIBN (azobisisobutyronitrile) as initiator. Measurements of absolute molecular weights and z-average radius of gyration of the produced copolymers have been performed for different polymerization times using a SEC system with coupled refractive index (RI) and multi-angle laser light scattering (MALLS) detectors.

The main difference between conventional free radical polymerization (FRP) and NMRP is due to the dynamic equilibrium described by Eq. (1), where $-\mathrm{P}^{\bullet}$ represents an active polymer radical, X a stable radical (e. g. TEMPO) and $-\mathrm{P}-\mathrm{X}$ a dormant alkoxyamine:

$$-\mathrm{P}^{\bullet} + \mathrm{X} \underset{k_{act}}{\overset{k_{deact}}{\rightleftharpoons}} -\mathrm{P}-\mathrm{X} \tag{1}$$

This intermittent equilibrium reduces substantially the concentration of active radicals and concomitantly the probability of termination. Consequently, the expected life time (t_l) of a polymer molecule in NMRP attains several hours, in contrast with the few seconds characteristic of FRP, as described by Eq. (2):

$$t_l = \frac{R}{r_t} \simeq \frac{1}{2k_t R} \tag{2}$$

with R representing the concentration of active radicals, r_t the rate of termination and k_t the correspondent rate coefficient. Is therefore possible to reduce the frequency of termination of polymer chains to levels below 5% , the result being a huge increase in the homogeneity of the products. Nowadays, besides NMRP other CRP techniques like Atom Transfer Radical Polymerization (ATRP) or Reversible Addition-Fragmentation Chain Transfer Polymerization (RAFT) are used with the aim of synthesizing

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more homogeneous linear polymers. More recently these concepts have been extended to non-linear polymerizations by trying to obtain also more homogeneous polymer networks with potential applications as advanced materials (Ide and Fukuda, 1997, 1999; Achilleos et al., 2007; Gao et al., 2008). Considering the NMRP of S/DVB, here we also show that a recently developed general kinetic approach can be used to assist in the design of such branched polymers.

Experimental Part

Experiments were carried out at 1 dm^3 scale using a 2.5 dm^3 maximum capacity stainless steel semi-batch reactor which has been described in detail elsewhere (Gonçalves et al., 2007). In this work the reactor was operated only in batch mode. Xylene at 98.5% purity, AIBN at 98% purity, TEMPO at 98% purity, styrene stabilized with 0.005% w/w 4-tert-butylcatechol at 99% purity and commercial grade divinylbenzene stabilized with 0.1% w/w 4-tert-butylcatechol at 80% purity have been purchased from Sigma Aldrich and used as received. That commercial DVB is a mixture of isomers, comprising 56.2% m-divinylbenzene and 24.2% p-divinylbenzene, plus 19.6% of ethylvinylbenzene. Xylene solvent is also a mixture of xylenes plus ethylbenzene ($\leq$ 25% in the latter component). Typically, NMRP and conventional S/DVB copolymerizations were carried out as follows: the empty reactor was purged with an argon stream (40 cm^3/min) and the heating process in order to reach 130 °C was started. After 15 min, the predetermined amounts of styrene, xylene, divinylbenzene and TEMPO (in NMRP experiments) were charged to the reactor. Until completion of the heating process the polymerization system was bubbled with argon at a flow rate of 40 cm^3/min. Owing to energy losses and insufficient heating power, around 100 and 120 min were needed to reach the set-point temperature of 130 °C in the conventional and NMRP experiments, respectively. This difference is caused by the heat generated by the auto-initiation of styrene in the conventional runs during the heating period. When the set-point was reached, samples of polymer were withdrawn from the reactor to be analyzed by SEC/RI/MALLS and immediately afterwards AIBN was added to the system, defining the initial time of the polymerization $t = 0$. The analysis of these samples has confirmed the existence of some thermal initiation of styrene during the heating process in conventional runs (monomer conversion of about 4 % was experimentally measured) and conversely, the absence of this phenomenon in the NMRP experiments has been found. After $t = 0$ samples of polymer were withdrawn from the reactor at prescribed polymerization times and analyzed by SEC/RI/MALLS. During the polymerization process the flow rate of the argon stream spargeing the system was reduced to 20 mL/min in order to prevent appreciable mass losses from the reactor, since it is operated at atmospheric pressure and the polymerization temperature is close to the xylene boiling point (around 140 °C).

Kinetic Modeling

Based upon a work started in the early nineties (Costa and Dias, 1994), it has been recently shown that molecular size distributions (MSD), sequence size distributions (SSD) and *z*-average radius of gyration distributions (RGD) can be predicted for complex irreversible non-linear polymerization systems (Costa and Dias, 2005, 2007; Dias and Costa, 2006, 2007). Besides the detailed molecular architecture which becomes feasible to describe, this general kinetic approach is valid for different kinds of reactors (batch, plug flow, semi-batch or CSTR) and is free of several mathematical simplifications with non-universal applicability. Moreover, this approach allows the development of a computational tool that can be used to simulate different polymerization systems in an automated fashion. Eqs. (3), (4) and (5) are the general master equations allowing the prediction of the MSD, SSD and RGD after specification of the chemical

Table 1: Chemical groups and kinetic scheme considered in the modeling studies of NMRP of S/DVB.

Chemical Groups	Chemical Reactions
Five Monomers: S, *m*-DVB, *p*-DVB and pendant double bonds (*m*-PDB, *p*-PDB). Five kinds of polymer growing Radicals. Five kinds of polymer dormant Radicals. Initiator, primary radicals from initiator, from monomeric styrene and from the dimer. Two kinds of dormant primary radicals and saturated nitroxyl radical. Nitroxyl radical (TEMPO), Dimer of Styrene, solvent and correspondent primary radical.	Mayo Dimerization of Styrene. Thermal Initiation of Styrene. Initiator Decomposition. Living/dormant exchange of radicals. Initiations of monomers and pendant double bonds. Chain transfers to monomers, solvent, dimer and initiator.

groups and kinetic scheme of the polymerization system.

$$\frac{\partial G}{\partial t} = G_{\mathcal{R}_P} + \frac{G_F(t) - G}{\tau} - \mathcal{R}_v G; \qquad G_{|t=0} = G_0\left[\mathbf{s_0}(t, \mathbf{s})\right] \tag{3}$$

$$\frac{\partial U}{\partial t} = G_{\mathcal{R}_S} + \frac{U_F(t) - U}{\tau} - \mathcal{R}_v U; \qquad U_{|t=0} = U_0\left[\mathbf{s}_0(t, \mathbf{s})\right] \tag{4}$$

$$\frac{\partial G_n^H}{\partial t} = G_{\mathcal{R}_{H_n}} + \frac{G_{n\,F}^H(t) - G_n^H}{\tau} - \mathcal{R}_v G_n^H; \qquad G_{n\,|t=0}^H = G_{n\,0}^H\left[\mathbf{s_0}^-(t, \mathbf{s}^-), \mathbf{s_0}^+(t, \mathbf{s}^+)\right] \tag{5}$$

In the present polymerization system, modeling studies were performed considering a kinetic scheme comprising a total of 36 chemical groups and 125 different chemical reactions, as briefly summarized in Table 1. Note that due to the existence of two isomers in commercial DVB, this polymerization system becomes more complex than a crosslinking process involving for instance pure diacrylates or dimethacrylates. Indeed, *m*-DVB, *p*-DVB and the correspondent pendant double bonds (*m*-PDB and *p*-PDB, respectively) have different reactivities (Gonçalves et al. (2007) and references therein) and therefore must be distinguished in the kinetic modeling. Moreover, due to the relatively high polymerization temperature (130 °C) which is required, other complex details arising from the thermal initiation of styrene must be taken into account in the present studies.

Results and Discussion

In Figure 1(a) is presented a typical kinetic plot showing the living character of a NMRP run. The modified monomer conversion $ln(M_0/M) = -ln(1-p)$ should roughly (after an initiation period) follow a linear growth with reaction time and this is confirmed with the experimental measurements presented in Figure 1(a). The predicted values were obtained using kinetic parameters available in the literature for linear NMRP polymerization systems (Zhang and Ray (2002), Fu et al. (2007) and references therein). Note that monomer conversion is almost not affected by the reactivities of *m*-PDB and *p*-PDB, since the concentrations of these species in the polymerization system is very low.

Figure 1(b) shows in detail the improved control of the molecular architecture achievable in NMRP synthesized polystyrene (PS) samples as compared to the FRP products. From the chromatograms of PS samples with different polymerization times shown in Figure 1(c) it is possible to observe the growth of molecular weights without concomitant broadening of the distribution. In fact, linear products with an

approximately constant polydispersity index (around 1.1) can be produced at increasing polymerization times (monomer conversions) using the NMRP technique.

Measured and predicted time evolution of $\overline{M}_n$ and $\overline{M}_w$ in a NMRP copolymerization of S/DVB with $y_{DVB} = 0.5\%$ and initial molar ratio TEMPO/AIBN=1.1 are presented in Figure 1(d). A good agreement between experimental observations and predictions is here observed using the reactivity of pendant double bonds as fitting parameters. It was estimated that the apparent reactivity ratio of PDB comparatively to styrene is $r = k_p^*/k_{p11} = 0.35$ (similar to the one found in Gonçalves et al. (2007) with FRP of S/DVB). It is plausible that the value of this reactivity ratio becomes affected by the effect of intramolecular cyclization reactions which were neglected in the present calculations. Indeed, these effects should be more important at 50% dilution as compared with bulk conditions used to estimate the equal reactivity of pendant vinyls in related works (Ide and Fukuda, 1997). An apparent decrease of the reactivity ratios of pendant vinyls with respect to the monomers has been found by these authors (Trigo et al., 2008) and other research groups (Gao et al., 2008) for other polymerization systems at diluted conditions, namely dimethacrylates and diacrylates, respectively.

Figure 1(e) compares the observed and predicted evolution of $\overline{M}_w$ for linear and non-linear polymer formation. The well-known linear growth of $\overline{M}_w$ for linear polystyrene does not occur with S/DVB copolymerization owing to the build-up of branched products. These results show that non-linear copolymerizations can be used to modify the properties of linear polymers with the goal of producing advanced materials (such as hyperbranched polymers). Figure 1(f) shows in detail the impact on the polymer molecular sizes of the presence of a small amount of DVB (about 0.5% mole fraction) in the NMRP polymerization system. A fraction of polymer molecules of molecular architecture close to linear polystyrene is present (showing an ill-separated peak at higher elution times) but most of polymer is branched.

Figure 2 compares experimental measurements (by SEC/MALLS) and theoretical predictions of the z-average radius of gyration of these non-linear polymers. This confirms the usefulness of the proposed kinetic approach namely to design with improved detail the molecular architecture of such materials. Note that results presented in Figure 2(b) show a more compact structure of NMRP S/DVB copolymers as compared with the FRP analogues. This means that the properties of these polymers can be manipulated in a known way through the use of CRP techniques.

Conclusions

Molecular architecture of NMRP S/DVB copolymers measured by SEC/MALLS shows important differences not only when compared with the linear case but also with respect to the FRP of the same monomers. It has now been shown that a recently developed general kinetic approach can deal with the complexities of this polymerization system, namely those caused by the huge number of different chemical species and involved reactions. The final goal of this research is to design hyperbranched polymers and networks with a well defined structure (which should be predicted by appropriate theoretical means) to be used for biomedical purposes or exploited as advanced materials. Earlier works on similar chemical systems (Ide and Fukuda, 1997) have now been extended with predictions and measurements of average molecular weights and radius of gyration of sol fraction. Likely influence of intramolecular reactions has been detected at 50 % dilution, showing that at best only in bulk conditions more or less ideal networks can be produced. Ongoing researches are expected to provide more assertive results.

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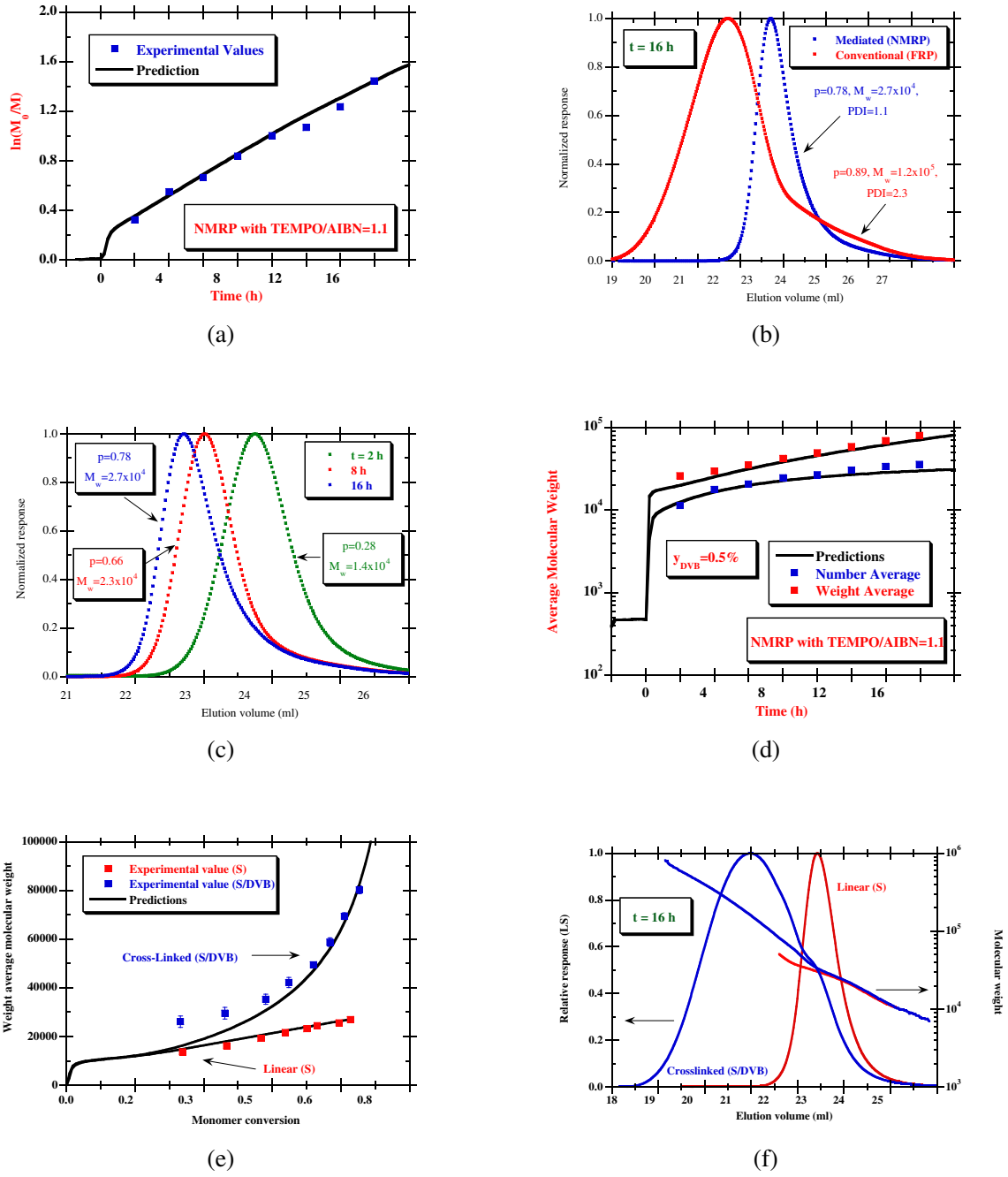
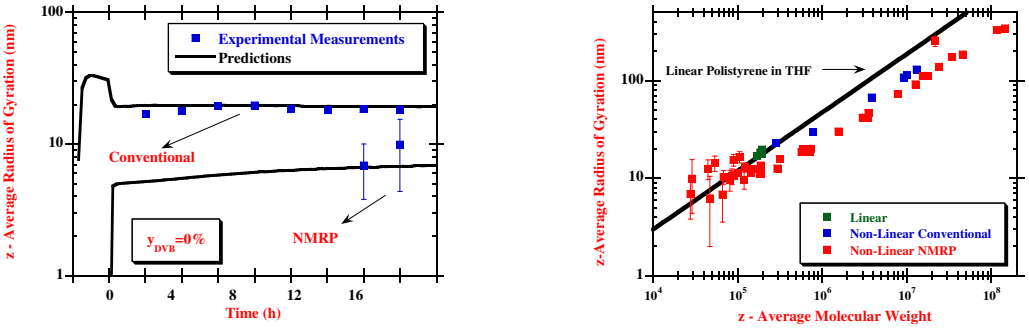


Figure 1: (a) Kinetic plot showing the living character of a NMRP run with TEMPO/AIBN=1.1. (b) Observed chromatograms (RI) of polystyrene (PS) samples synthesized at 130 °C using conventional free radical polymerization (FRP) and NMRP. In both cases the polymerization time is $t = 16$ h. Polymerizations in S/X solution (50 % v/v) using the same initial ratio S/AIBN in both runs: $S_0 = 4.4$, $AIBN_0 = 0.0086$ and $TEMPO_0 = 0.0096$ mol dm^{-3} (NMRP experiment). (c) Observed chromatograms of NMRP synthesized PS samples (same conditions as (b)) with different polymerization times showing the growth of MW without concomitant broadening of the distribution (PDI around 1.1). (d) Measured and predicted time evolution of $\overline{M}_n$ and $\overline{M}_w$ in a NMRP copolymerization of S/DVB with $y_{DVB} = 0.5\%$ and initial molar ratio TEMPO/AIBN=1.1. (e) Predicted and measured $\overline{M}_w$ in linear (S) and non-linear (S/DVB) NMRP polymerizations. (f) Observed chromatograms (MALLS) of PS and S/DVB samples synthesized using NMRP. Copolymerization S/DVB was performed with $DVB_0 = 0.022$ mol dm^{-3}.



(a) (b)

Figure 2: (a) Predictions and experimental observations for $\overline{R}_g$ in conventional and NMRP linear runs. (b) Experimentally observed relation $\overline{R}_g$ vs. $\overline{M}_z$ in different conventional and NMRP runs in the S/DVB copolymerization.

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