Kinetic Modeling of the Suspension Copolymerization of Styrene/Divinylbenzene with Gel Formation

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Summary: Experimental and theoretical studies concerning the suspension copolymerization of styrene with divinylbenzene are reported. Experiments were carried out in a batch stirred reactor, at 1.2 dm³ scale, and extended beyond gelation in order to synthesize insoluble material. Looking for real time information concerning the building process of such materials, these polymerizations were *In-line* monitored using a FTIR-ATR immersion probe. Polymer samples collected before and after gelation were *Off-line* characterized using a SEC/RI/MALLS system allowing the measurement of monomer conversion, average molecular weights, MWD and also the z-average radius of gyration. The weight fraction of insoluble material (gel) was measured for samples with different reaction times. The experimental program has included the study of the influence of key polymerization parameters on the dynamics of gelation and some properties of the resulting networks, namely the initial mole fraction of crosslinker and the initial proportions between monomers and inert diluent. Variable *n*-heptane/toluene mixtures were used within this purpose. These experimental observations were complemented with theoretical studies using a general kinetic approach allowing the prediction of MWD and z-average radius of gyration before and also after gelation. Comparison of the experimental measurements with these predictions is being exploited to develop modeling tools useful for the design of operating conditions allowing the improvement of the performance of the final products.

Keywords: gels; kinetics (polym.); modeling

Introduction

A few insoluble polymer networks can be used as advanced materials due to the sensitivity of their microscopic properties to external stimulations. These polymers are often classified as stimuli responsive or *smart polymers*. Applications of these kinds of materials in biomedicine or bionanotechnology is nowadays a subject attracting considerable research efforts. Huge swelling ratios are also observed in many gels which is explored to produce superabsorbent materials. Formation of macroporous structures in polymer networks also makes possible their use as particles and membranes for many separation processes.

Styrene/divinylbenzene gels (S/DVB) are well-known for that purpose, usually after chemical derivatizing, such as for the ubiquitous ion-exchange resins. The formation of insoluble networks based on these monomers was studied by Staudinger and Huseman[1] at the very beginning of the development of polymer science.[2] Three stages can be identified in the time-line concerning the improvement of the production of S/DVB gel beads:

- Studies on the manipulation of the swelling ratio of the particles by adjusting the amount of DVB in the polymerization system.

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- Improved materials with a macroporous structure were obtained by suspension polymerization of S/DVB in the presence of an inert diluent. Phase separation during this process is the main source for the formation of pores in the resulting materials, even in the dry state.[2–6] Macrosyneresis (macroscale) and microsyneresis (microscale) phase separation during the crosslinking process depend on the synthesis conditions. This can be exploited in order to design the porous structures of the materials. Specially important in this context are the works of K. Dusek and co-workers (see [2] and references therein), which have lead to major contributions to the knowledge of the macroporous networks based on the crosslinking of vinyl/divinyl monomers.

- The study of the formation of elastically ineffective crosslinks due to cyclization and multiple crosslinks, existence of trapped radicals and the role of pendant vinyl groups, among others.[7–16] Nowadays, these issues are still being actively investigated by different research groups.

As above described, several important research works concerning the synthesis of gel beads through the conventional radical polymerization of S/DVB were carried out along the last decades. An extensive list of works dealing with this subject can be found in the review by O. Okay.[2] The present work is focused in the dynamics of formation of such gel beads in a batch reactor, with the goal of obtaining new insights in the polymer reaction engineering of such processes. The experimental program has covered the synthesis and characterization of polymer networks, both in the pre- and post-gelation periods. Final materials were also characterized by SEM. These experiments are complemented with kinetic modeling studies in the framework of a general theory which can be used before and after gelation.[7–16] Recent studies of this research team concerning the modeling of FRP and CRP of vinyl/divinyl monomers leading to soluble materials[17–20] are now extended with experiments on the post-gelation period here reported for the first time.

Experimental Part

Materials

Styrene of 99% purity stabilized with 0.005% w/w 4-tert-butylcatechol, commercial grade of divinylbenzene of 80% purity stabilized with 0.1% w/w 4-tert-butylcatechol, AIBN of 98% purity, toluene of 99.7% purity and *n*-heptane of 99% purity were purchased from Sigma Aldrich and used as received. Commercial DVB used in the present work is a mixture of isomers: 56.2% *m*-divinylbenzene, 24.2% *p*-divinylbenzene plus 19.6% of ethylvinylbenzene. Poly(vinyl alcohol) (PVA) with $\overline{M}_w$ of 85000-124000, 87-89% hydrolyzed, also from Sigma-Aldrich was used as a dispersant. Suspensions were prepared using deionized water.

Suspension Polymerizations

A detailed description of the experimental set-up used in this work can be found elsewhere.[17] An excess of aqueous phase, containing PVA, was previously prepared by dissolving the appropriated amount of surfactant in deionized water, at room temperature, using a magnetic stirrer. The concentration of PVA in aqueous phase was set using the total monomer weight as reference. In all experiments 0.09% of PVA by total monomer weight was used, similarly to the reported in related works.[3] The desired quantity of aqueous phase (around 913 mL) was charged to the reactor and brought to the polymerization temperature (60 °C) with the mechanical stirrer working at 400 rpm. The polymerization medium was purged with argon at a flow rate of 40 cm^3/min before and during the operation. The organic phase was prepared by forming a solution involving the required amounts of chemicals, namely: styrene, divinylbenzene, AIBN, *n*-heptane and toluene, as detailed in Table 1. This solution was prepared immediately before the polymerization, at room temperature, in

Table 1.
Description of a set of experiments performed in the study of the suspension copolymerization of Styrene/divinylbenzene at 60 °C.

Run	V_T (dm³)	f_{OR}	f_M	f_{DVB}	$100 \times f_I$	f_{HEP}
1	1.2	0.24	0.5	0.2	1.24	0.00
2	1.2	0.24	0.5	0.2	1.25	0.25
3	1.2	0.24	0.5	0.2	1.25	0.50
4	1.2	0.24	0.5	0.2	1.24	0.75
5	1.2	0.24	0.5	0.2	1.25	1.00
6	1.2	0.24	0.5	0.1	1.25	0.50

order to minimize the thermal decomposition of AIBN. When the temperature setpoint for the aqueous phase was reached, the proper amount of organic phase (around 287 mL) was charged to the reactor defining the start of the polymerization. Product samples were collected from the reactor at prescribed polymerization times. All polymerizations were stopped after 6 hours of reaction.

In-Line FTIR-ATR Monitoring

These polymerizations were *in-line* monitored using an Attenuated Total Reflection (ATR) immersion probe coupled to a Fourier Transform Infra-Red (FTIR) spectrophotometer. The following instruments were used: Axiom Analytical immersion probe, model DPR207 (ZnSe element, spectral cutoff at $600\,cm^{-1}$, maximum pressure and temperature operation 60 bar and 280 °C, respectively) and an ABB Bomem Fourier Transform Infra-Red (FTIR) spectrophotometer, model FTLA2000-104. The probe and the spectrophotometer are connected by a three arms light guide and an ABB Bomem Mercury-Cadmium Telluride (MCT) detector (model D10B), cooled with liquid nitrogen, equips the spectrometer in order to increase the sensitivity of the analysis. These ATR-FTIR measurements were performed using the spectrum of air taken at room temperature as the reference background being the optical system continuously flushed with argon. A resolution of $4\,cm^{-1}$ was used for the spectra that were taken over the full MIR range from $600\,cm^{-1}$ to $4000\,cm^{-1}$. Each spectrum was calculated from 128 interferograms.

SEC/RI/MALLS Products Characterization

Samples collected from the reactor at different polymerization times, including aqueous and organic phases, were poured in a decanting ampoule containing a large quantity cold water in order to stop the reaction. After decanting, most of the organic phase was diluted in a large amount of methanol in order to precipitate the polymer (soluble and insoluble fractions). For samples collected before gelation, a small amount of organic phase was directly diluted in THF and analysed by SEC/RI/MALLS. With samples containing gel, the soluble fraction analyzed by SEC/RI/MALLS was obtained after the immersion of the global material in THF, during one day, as described below. The same instruments described in our past works[17–20] were here used for this purpose. Time evolution of polymer molecular weight and z-average radius of gyration of the soluble fraction were thus measured, before and after gelation, for the set of experiments performed.

Measurement of the Weight Fraction of Gel

Polymer samples (soluble and insoluble fractions) obtained by precipitation in methanol were filtrated and dried in vacuum overnight. Afterwards, they were washed several times (during one week) in large amounts of THF in order to collect the insoluble network. The time evolution of the insoluble weight fraction of polymer (gel) during the polymerizations was thus measured.

Swelling Ratio Measurements

For each run, the final suspension, correspondent to 6 hours of polymerization, was processed as above described in order to isolate the produced gel beads. The swelling ratio of the dried gel beads was estimated by weighing around 1 g of material which was afterwards immersed in a large amount of THF. After 24 hours, the swollen gel beads were weighed again and the ratio between swollen and dried weights was used to estimate the swelling ratio of these materials.

Scanning Electron Microscopy (SEM)

The dried gel beads above described were also analyzed by Scanning Electron Microscopy (SEM) in the Centro de Microscopia da Universidade do Porto (CEMUP). Th influence of the synthesis conditions in the structure of the produced materials (e.g. macroporous formation) could thus be assessed.

Kinetic Modeling

The kinetic scheme considered in the modeling studies here performed is described by Equations (1)-(12) with I representing the initiator (AIBN), R_0 the primary radicals and M_1, M_2 and M_3 the three monomers (styrene, *m*-divinylbenzene and *p*-divinylbenzene, respectively). Polymer molecules bearing k radicals, m pendant double bonds (PDB) and n repeating units or monomer moieties (degree of polymerization) are represented by $P_{k,m,n}$; the counts of the repeating units derived from the three monomers have been lumped. This simple description of the polymer chains structure is used in order to keep this presentation within a manageable size. The general kinetic approach used in the present work[7–16] is able to accommodate more complex descriptions of non-linear polymerization systems, namely the simultaneous consideration of several different kinds of polymer radicals and other reaction sites, encompassing also the detailed prediction of the molecular architecture of polymer chains. These distinctive features of this theoretical approach were recently applied to the analysis of different non-linear polymerization systems involving styrenic, acrylate and methacrylate monomers and in the framework of classical and controlled radical polymerization, namely NMRP and ATRP.[17–20] Despite the simplicity of the kinetic scheme here considered, it is shown below that the most important features of the present polymerization system can be captured by the simulations performed. The lack of explicit consideration of intramolecular cyclization reactions (mostly propagations and terminations) is the major drawback of this kinetic scheme, as also discussed below.

AIBN decomposition:

$$I \xrightarrow{k_d} 2f\, R_0 \tag{1}$$

Styrene initiation:

$$R_0 + M_1 \xrightarrow{k_{I1}} P_{1,0,1} \tag{2}$$

m-divinylbenzene initiation:

$$R_0 + M_2 \xrightarrow{k_{I2}} P_{1,1,1} \tag{3}$$

p-divinylbenzene initiation:

$$R_0 + M_3 \xrightarrow{k_{I3}} P_{1,1,1} \tag{4}$$

PDB initiation:

$$R_0 + P_{k,m,n} \xrightarrow{k_{I4}} P_{k+1,m-1,n} \tag{5}$$

Styrene propagation:

$$P_{k,m,n} + M_1 \xrightarrow{k_{p1}} P_{k,m,n+1} \tag{6}$$

m-divinylbenzene propagation:

$$P_{k,m,n} + M_2 \xrightarrow{k_{p2}} P_{k,m+1,n+1} \tag{7}$$

p-divinylbenzene propagation:

$$P_{k,m,n} + M_3 \xrightarrow{k_{p3}} P_{k,m+1,n+1} \tag{8}$$
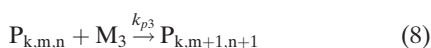
PDB propagation (crosslinking):

$$P_{k,m,n} + P_{k',m',n'} \xrightarrow{k_{p4}} P_{k+k',m+m'-1,n+n'} \tag{9}$$

Chain transfer to solvent:

$$P_{k,m,n} + S \xrightarrow{k_S} P_{k-1,m,n} + R_0 \tag{10}$$

Termination by combination:

$$P_{k,m,n} + P_{k',m',n'} \xrightarrow{k_{tc}} P_{k+k'-2,m+m',n+n'} \tag{11}$$
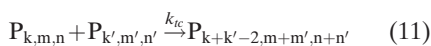
Termination by dismutation:

$$P_{k,m,n} + P_{k',m',n'} \xrightarrow{k_{td}} P_{k-1,m,n} + P_{k'-1,m,n} \tag{12}$$
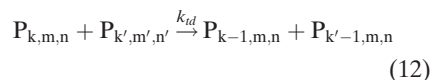
Most of the kinetic parameters used in the simulations have been collected from other research works, namely for what concerns the decomposition rate of AIBN at $60\,°C$, $k_d = 9.6 \times 10^{-6}\,s^{-1}$ with $f = 0.6$ and styrene polymerization, $k_{p1} = 340\,dm^3 mol^{-1} s^{-1}$, of which detailed bibliographic sources have been presented elsewhere.[17] Specially

important in the present context are the reactivity ratios of m- and p-divinylbenzene with styrene, and the values $r_{12} = k_{p1}/k_{p2} = 0.43$, $r_{13} = k_{p1}/k_{p3} = 0.24$, previously measured for these pairs were also here considered.[21] Chain transfer to solvent and termination were quantified using the same kinetic parameters before used for the solution polymerization of the same chemical system: $C_S = k_S/k_{p1} = 0.12 \times 10^{-4}$, $k_{p1}/\sqrt{k_t} = 0.035$ $(dm^3 mol^{-1} s^{-1})^{1/2}$, $\alpha_{tc} = k_{tc}/k_t = 0.95$.[17] The rate constants of initiation reactions were considered to be equal to the correspondent propagation steps: $k_{Ij} = k_{pj}$. The rate constant for the propagation of pendant double bonds $(k_{p,4})$ was used as the single fitting parameter because, in the absence of intramolecular cyclizations, the crosslinking is the major mechanism governing the properties of the polymer networks, as it has been shown in previous works.[17–20]

Applying the principles of the general kinetic approach we have been developing[7–16] with the kinetic scheme described by Equations (1)-(12), the Population Balance Equation (PBE) in terms of Generating Functions (GF) below written is obtained:

$$
\begin{aligned}
\frac{\partial G}{\partial t} =\ & k_{p1}M_1(s{-}1)\frac{\partial G}{\partial s_R} + k_{p2}M_2(s_B s{-}1)\frac{\partial G}{\partial s_R} + k_{p3}M_3(s_B s{-}1)\frac{\partial G}{\partial s_R} \\
& + k_{p4}\left(\frac{1}{s_B}\frac{\partial G}{\partial s_R}\frac{\partial G}{\partial s_B} - B\frac{\partial G}{\partial s_R} - R\frac{\partial G}{\partial s_B}\right) + k_{tc}\left[\frac{1}{s_R^2}\left(\frac{\partial G}{\partial s_R}\right)^2 - 2R\frac{\partial G}{\partial s_R}\right] \\
& + 2k_{td}R\left(\frac{1}{s_R}{-}1\right)\frac{\partial G}{\partial s_R} + k_S S\left(\frac{1}{s_R}{-}1\right)\frac{\partial G}{\partial s_R} + k_{I1}R_0 M_1 s_R s \\
& + k_{I2}R_0 M_2 s_R s_B s + k_{I3}R_0 M_3 s_R s_B s + k_{I4}R_0\left(\frac{s_R}{s_B}{-}1\right)\frac{\partial G}{\partial s_B}
\end{aligned}
$$

(13)

The generating function of mole concentrations of polymer species with respect to the counts of chemical groups is here defined by:

$$
G(s_R, s_B, s) = \sum_{k=0}^{\infty}\sum_{m=0}^{\infty}\sum_{n=0}^{\infty} P(k,m,n)s_R^k s_B^m s^n
$$

(14)

Laplace parameters of the GF of polymer population named s_R, s_B and s are associated with the counts of radicals in polymer molecules (k), of PDB (m) and repeating units (n), respectively. In PBE

Equation (13), R and B represent the total concentration of polymer radicals and pendant double bonds, respectively. As no polymer exists in the system when the reaction starts, the initial condition of Equation (13) is:

$$
G|_{t=0} = 0
$$

(15)

Solution of PBEs of the kind of Equation (13) can be obtained by the method of the characteristics.[7–16] Before gelation, the problem reduces to a system of ordinary differential equations with initial conditions (IVP) and gelation point is located through the divergence of the solution of this IVP problem. After gelation, two-point boundary value problems (TPBVP) must be solved in order to obtain the properties of soluble and non-soluble fractions. The techniques described elsewhere[7–16] were used to obtain the results presented below.

Results and Discussion

Figure 1 shows the predicted and observed time evolution of the weight average molecular weight $(\overline{M}_w)$ during the suspension copolymerization of S/DVB at $60\,°C$ (see Table 1). Experimental values were measured before and after gelation by SEC/RI/MALLS, as above described. The effect of the mole fraction of DVB in the initial monomer mixture $(f_{DVB} = 10$ and $20\%)$ on the dynamics of $\overline{M}_w$ in batch reactor is clearly put into evidence, namely for what concerns the delay in gelation time. This dynamics was also predicted before and after gelation using the aforementioned calculation techniques. A good agreement between measurements and predictions can
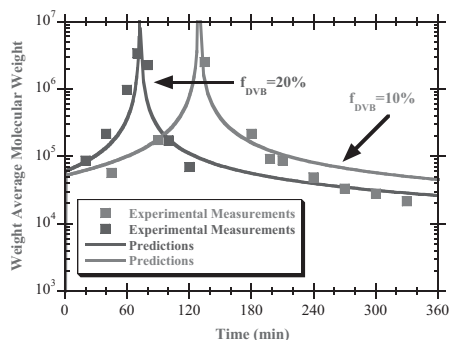
Figure 1.

Predicted and measured time evolution of the weight average molecular weight ($\overline{M}_w$) during the suspension copolymerization of S/DVB at 60 °C. The effect of the mole fraction of DVB in the initial monomer mixture (f_{DVB} = 10 and 20%) over the dynamics of $\overline{M}_w$ in batch reactor is observed. This dynamics was predicted and measured before and also after gelation.

Figure 2.

Predicted and measured time evolution of the weight fraction of gel (w_g) during the suspension copolymerization of S/DVB at 60 °C. The effect of the mole fraction of DVB in the initial monomer mixture (f_{DVB} = 10 and 20%) over the dynamics of w_g is observed. Experimental measurements are confined between the predictions correspondent to the ideal crosslinking (C_{PDB} = 1, absence of intramolecular cyclizations) and the non-ideal behavior (C_{PDB} < 1) considering the same reactivity ratios obtained from the fitting of average molecular weight.

be obtained if the reactivity of PDB is used as a fitting parameter. In this context the following reactivity ratios of PDB comparatively to styrene were estimated: $C_{PDB} = k_{p4}/k_{p1} = 0.055$ for f_{DVB} = 20% and $C_{PDB} = 0.07$ for f_{DVB} = 10%. These unrealistic low values obtained by the fitting procedure are a consequence of neglecting intramolecular cyclizations, which are a competitive kinetic mechanism decreasing crosslinking efficiency, as previously shown.[17–20] The slightly different values of the reactivity ratios of PDB estimated for f_{DVB} = 20% and f_{DVB} = 10% are also probably a result of the different impact of intramolecular cyclizations which, for the same dilution, should increase with the initial mole fraction of DVB. Simple attempts to include intramolecular cyclizations in the framework of the present kinetic approach have already been performed[12] but a lot more additional theoretical developments are needed in this context. Despite this limitation, results presented in Figure 1 show that some important features of gel formation can be captured by the simple kinetic scheme here considered.

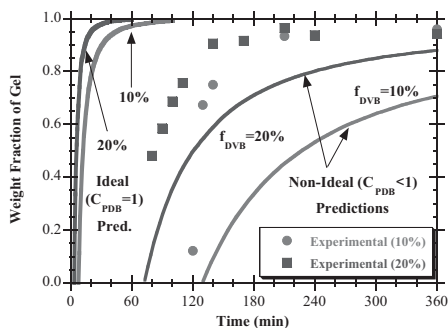Figure 2 shows a comparison between the predicted and measured time evolution of the weight fraction of gel (w_g) during the suspension copolymerization of S/DVB. In this case, high deviations between the measured values and predictions are observed for both initial compositions. The same kinetic parameters resulting from the fitting studies described in Figure 1 were used in the calculation of w_g considering a non-ideal crosslinking process (C_{PDB} < 1). The ideal behavior correspondent to C_{PDB} = 1 (ideal crosslinking in the absence of intramolecular cyclizations) is also presented in Figure 2. Experimental measurements are confined between the predictions correspondent to these two simulation systems, confirming the modeling limitations before described (intramolecular cyclizations not included). In fact, the produced gels were several times washed in THF and only small amounts of sol are expected to be entrapped in the final products given the not so large molecular weight. Therefore, deficient gel washing can not explain the huge differences observed. Formation of microgel and inhomogeneous gel structures along polymerization can be at the source of such

discrepancies, with intramolecular cyclizations playing a major role. These phenomena were not taken in to account in the present modeling studies (complex developments are needed) and the predicted gel fraction is underestimated for the non-ideal system and overestimated for the ideal crosslinking behavior. In the presence of very high contents of DVB (10 and 20%) and due to the relative small length of
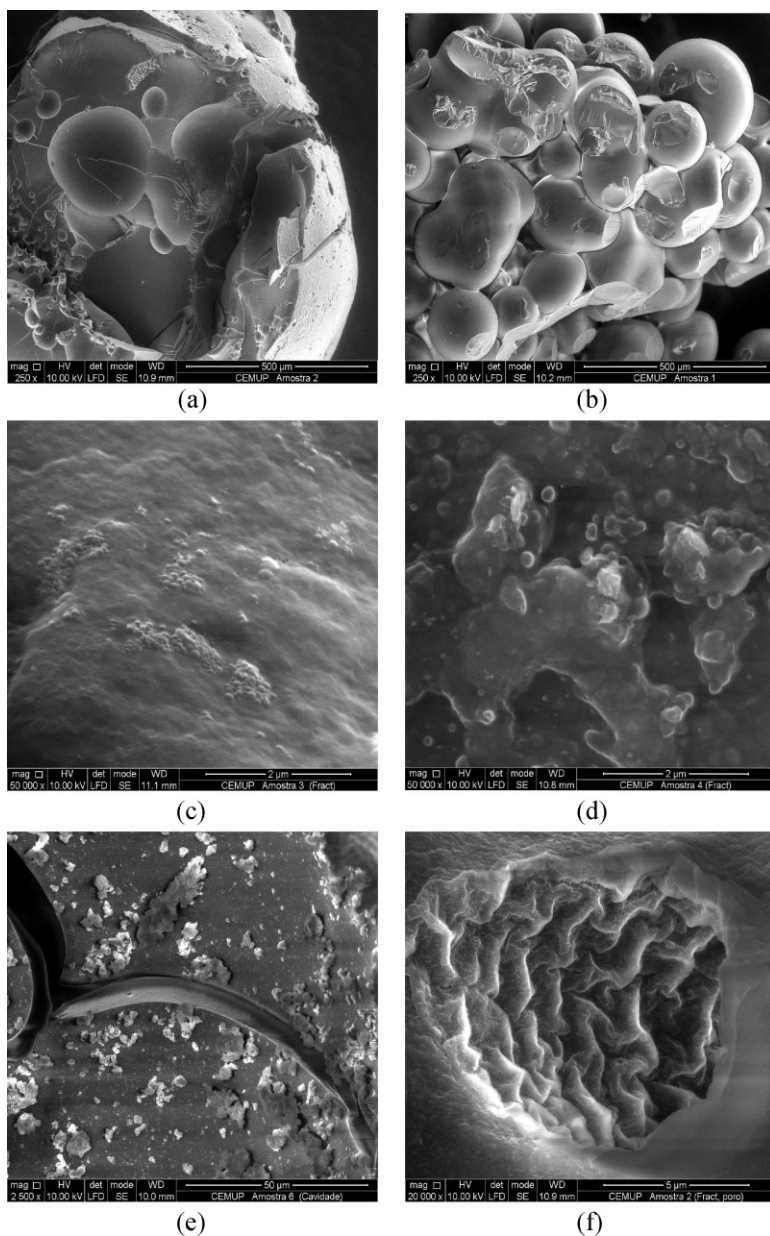

Figure 3.
(a) SEM of S/DVB gel beads obtained in run 3 with magnification of 250 ×. (b) Gel beads of run 6 with magnification of 250 ×. (c) Run 1 with magnification of 50000 ×. (d) Run 5 with magnification of 50000 ×. (e) Run 2 with magnification of 2500 ×. (f) Run 3 with magnification of 20000 ×.

primary chains (namely when compared with non-linear acrylic systems), intramolecular cyclizations phenomena are likely to occur in the formation of S/DVB networks. It is a relevant result from this work the finding that a simplistic model assuming reduced pendant bond reactivity is unable to predict both sol average molecular weight or radius of gyration and also sol fraction.

The influence of the synthesis conditions in the end-use properties of S/DVB gel beads was extensively studied in the last decades.[3–6] Experimental studies concerning the effects of initiator concentration, temperature, stirring speed, concentration of crosslinking agent, diluent concentration and thermodynamic affinity are reported in these works. The influence of these parameters in the gel beads appearance, namely concerning fusion and coalescence was also studied.[3] The morphology of the products obtained in the present research was also studied by Scanning Electron Microscopy (SEM) as shown in Figure 3, where the micrographs of S/DVB gel beads synthesized in different conditions (see Table 1) are presented. Comparison of Figures 3(a) and (b) puts into evidence the effect of the DVB content in bead formation. Higher DVB amounts seems to promote the formation of such structures, avoiding the synthesis of clustered and fused products.[3] The effect of the thermodynamic affinity of the diluent[4] with the copolymer can be observed by comparison of Figures 3(c) and (d) where runs with very different *n*-heptane/toluene ratios are analyzed. Gel beads prepared with a large fraction of bad solvent in the diluent (*n*-heptane in the present work) show very rough surfaces as observed in Figure 3(d). When the thermodynamic affinity of the diluent increases (higher proportion of toluene) gel beads produced have a smoother surface, characteristic of non-porous materials, as observed in Figure 3(c). Other details of the morphology of such materials can be observed in Figures 3(e) and (f) where a cavity and a macroporous structures are showed by SEM.
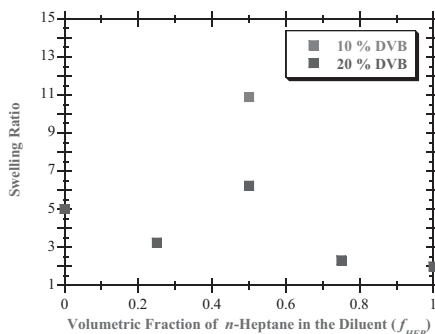

Figure 4.

Measured swelling ratio for S/DVB gel beads synthesized using different proportions of *n*-heptane/toluene in the organic phase and different initial mole fraction of DVB in the monomer mixture (see Table 1). The amount of DVB in the initial mixture and the diluent composition plays an important role in this end use property of the gel beads.

Figure 4 depicts the measured swelling ratio for S/DVB gel beads synthesized using different proportions of *n*-heptane/toluene in the organic phase and different initial mole fractions of DVB in the monomer mixture, as detailed in Table 1. Note that the amount of DVB in the initial mixture and the diluent composition plays an important role in this end use property of the gel beads. With the materials synthesized in the present work, a maximum swelling ratio around 11 was measured for gel beads produced with $f_{DVB} = 10\%$ and $f_{HEP} = 0.5$. The dependency of the swelling ratio of S/DVB gel beads on diluent, styrene and DVB concentrations used in the synthesis process has also been previously reported in other research works.[3]

In-line FTIR-ATR monitoring of vinyl monomer polymerization has been investigated in the last years driven by the need for improvement in product quality. The establishment of feed policies of monomers in semi-batch co- terpolymerizations, with an expected impact on the molecular architecture of linear polymers is such an application of *In-Line* FTIR-ATR monitoring. The determination of the reactivity ratios for different groups of vinyl monomers is also an important application of this technique. Several works reporting the

In-Line FTIR-ATR monitoring of homo-, co-, terpolymerizations using different operational conditions, namely emulsion and solution processes, can be found in the literature.[22–30] Suspension crosslinking copolymerizations performed in the present work were also monitored by *In-Line* FTIR-ATR, as previously described. Typical results obtained with that technique are presented in Figure 5. Our main goal with such in-line monitoring is to obtain real time information concerning the building process of the synthesized non-linear materials. The reactivity ratios of the involved vinyl monomers, divinyl monomers and PDBs are a valuable information in such context, as above discussed. Results presented in Figure 5 show the occurrence of a phenomenon similar to ''*catastrophic coagulation*'' reported for instance in the *in-line* monitoring of butyl acrylate/vinyl acetate emulsion copolymerization.[28] With emulsion processes, this phenomenon is due to unstable polymerization conditions which seems also to occur at the gel point for the suspension crosslinking polymerization performed in the present work. For the operation conditions used in the

present work, gelation occurs at low monomer conversion (around 10% with $f_{DVB} = 10\%$, as estimated by SEC/RI/MALLS) and by consequence ''*catastrophic coagulation*'' precluded the obtainment by *In-Line* FTIR-ATR of reliable quantitative information concerning the reactivity of the different monomers/pendant double bonds involved. Besides ''*catastrophic coagulation*'', is possible that the spectra observed with *In-Line* FTIR-ATR can also be a result of the coating of the ATR crystal during the polymerizations. Further experiments with different operation conditions (e.g. changing the kind of stabilizer, its concentration and agitation speed) must be performed to elucidate this issue with suspension polymerization. On other hand, *In-Line* FTIR-ATR monitoring of emulsion polymerization of vinyl monomers is reported is previous research works without apparent occurrence of coating of the ATR crystal.[22,28] However, given its very different initiation mechnism and likely occurence of space separation of radicals, emulsion polymerization is very different from the suspension polymerization operation here studied and major
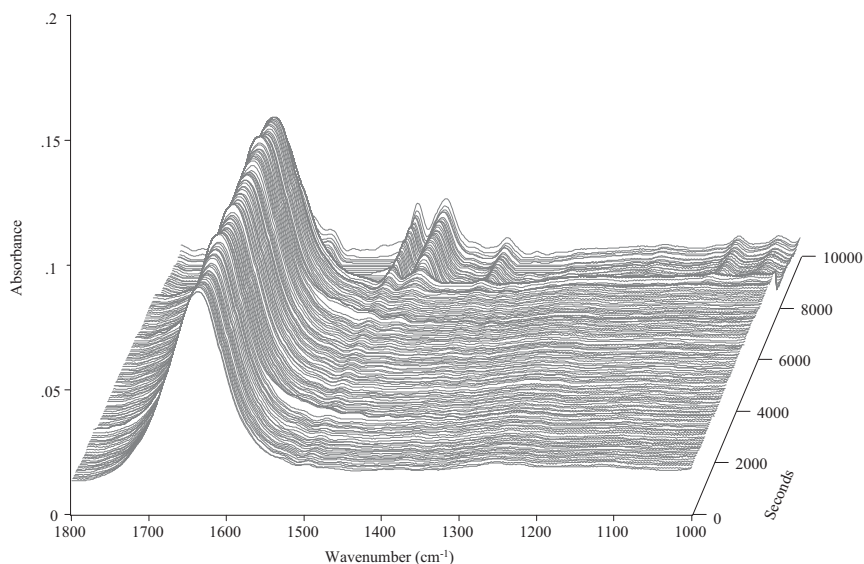

Figure 5.

FTIR-ATR spectra observed in the *in-line* monitoring of the suspension copopolymerization of S/DVB using *n*-heptane and toluene as diluents of the organic phase. The figure shows spectra with wavelength number from 700 to 1800 cm^{-1}. Changes in the spectrum due to "*catastrophic coagulation*" are also here visible.

modeling changes would have to be discussed. Use of confocal Raman spectroscopy (with a higher penetration depth) should overcome the coating of the ATR crystal in both circumstances (suspension/emulsion), but this requires major changes on the experimental set-up here used.

Conclusion

Suspension copolymerization of styrene/divinylbenzene with gel formation was experimentally studied by performing a set of different runs in a batch reactor. The dynamics of product molecular properties was measured by SEC/RI/MALLS. These reactions were also *In-Line* monitored by FTIR-ATR. The produced gel beads were analyzed by scanning electron microscopy (SEM) and the impact on the morphology of these materials of parameters such as the proportion of bad/good solvents in the diluent was studied. The dynamics of the gel fraction in batch reactor was followed and the swelling ratio of the resulting gel beads was also quantified. A general kinetic approach allowing predictions before and also after gelation was used in the modeling studies of this non-linear copolymerization system.

It was shown that the main features of this crosslinking process can be captured by the kinetic model developed using as a single fitting parameter the relative reactivity of the pendant double bonds. Under these circumstances, with the same set of kinetic parameters, it is possible obtain good predictions of the dynamics of $\overline{M}_w$ before and also after gelation, which is a major contribution of this work for the polymer reaction engineering of such processes. Nevertheless, the unrealistic low values of reactivity estimated (around 6% of styrene reactivity) should be mostly an effect of neglecting intramolecular cyclizations in the model.

SEM characterization of these gel beads confirmed the formation of macroporous structures if appropriated synthesis conditions are used, namely concerning the

thermodynamic affinity of the diluent mixture. In the present work, different proportions of *n*-heptane/toluene (bad/good solvents) were considered for this purpose. Measured swelling ratios of these gel beads are also in line with previous works and a maximum swelling ratio of 11 was here observed.

In-Line FTIR-ATR monitoring of the crosslinking process here performed showed the occurrence of *"catastrophic coagulation"* at the gel point which precluded the intended in-line measurement of the building parameters of the polymer networks. A new design operating conditions should be carried out in order to avoid this phenomenon so that this spectroscopic technique can be fully exploited.

The present work paves the way to further studies concerning the design and production of gel beads by means of different radical polymerization systems, namely nitroxide mediated radical polymerization (NMRP) of styrene/divinylbenzene. The exploitation of the distinctive features of the general kinetic approach here considered to improve properties of gels produced by CRP is an expected outcome of this research line. These new studies should go in parallel with the theoretical developments allowing the proper consideration of intramolecular cyclizations in the kinetic schemes, an issue which has once again been clearly identified in this work. Ongoing studies concerning the kinetic prediction of elastic properties of gels should also be specially useful in this context.

Notation

B	total concentration of polymer pendant double bonds.
$C_S = k_S/k_{p1}$	reactivity ratio for chain transfer to solvent.
$C_{PDB} = k_{p4}/k_{p1}$	reactivity ratio for polymerization of PDB.
f	initiator decomposition efficiency.
f_{DVB}	initial mole fraction of divinylbenzene in the total monomer content.

f_{HEP} volumetric fraction of n-heptane in the diluent mixture (n-heptane + toluene).

f_I initial mole ratio between initiator and total amount of monomers double bonds.

f_M initial volumetric fraction of monomers (styrene + divinylbenzene) in the organic phase (styrene + divinylbenzene + n-heptane + toluene).

f_{OR} initial volumetric fraction of organic phase in the total liquid content (organic phase + water).

$G(s_R, s_B, s)$ generating function of the distribution of mole concentrations of polymer species according to their counts of radicals, PDB and repeating units.

I concentration of initiator.

M_k concentration of monomer or macromonomer of the kind k.

$\overline{M}_w$ weight-average relative molecular mass.

k_d rate coefficient of the unimolecular thermal initiator decomposition.

k_{Ij} rate coefficient of the initiation of monomer or macromonomer of the kind j.

k_{pj} rate coefficient of the propagation of monomer or macromonomer of the kind j.

k_S rate coefficient of the chain transfer to solvent.

k_t rate coefficient of the global radical termination.

k_{tc} rate coefficient of the radical termination by combination.

k_{td} rate coefficient of the radical termination by disproportionation.

$P(k, m, n)$ concentration of polymer molecules bearing k radicals, m PDB and n repeating units.

r_{ij} polymerization reactivity ratio.

R_0 concentration of primary radicals.

R total concentration of polymer radicals.

s Laplace parameter of the generating function associated with the count of the number of repeating units.

s_B Laplace parameter of the generating function associated with the count of the number of PDB.

s_R Laplace parameter of the generating function associated with the count of the number of polymer radicals.

t time.

T temperature.

V_T total liquid volume in the reactor, including water and organic phase.

w_g weight fraction of gel.

Greek Characters

α_{tc} relative rate of radical termination by combination.

α_{td} relative rate of radical termination by disproportionation.

Subscripts

n number average.

w weight average.

z z-average.

0 initial.

Abbreviations

AIBN 2,2′-azobis(2-methylpropionitrile).

ATR Attenuated Total Reflection.

ATRP atom transfer radical polymerization.

CRP controlled radical polymerization.

DMF	*N,N*-dimethylformamide.
DVB	divinylbenzene.
FRP	free radical polymerization.
FTIR	Fourier Transform Infra-Red.
GF	generating function.
IVP	initial value problem.
M_k	monomer or macromonomer of the kind k.
MCT	mercury-cadmium-telluride detector.
MIR	medium Infra-Red.
MWD	molecular weight distribution.
NMRP	nitroxide-mediated radical polymerization.
ODE	ordinary differential equation.
PBE	population balance equation.
PDB	pendent double bond.
PDE	partial differential equation.
PVA	poly(vinyl alcohol).
$P_{k,m,n}$	polymer molecule bearing k radicals, m PDB and n repeating units.
R_0	primary radical.
S	styrene.
SEC/RI/ MALLS	size exclusion chromatography with refractive index and multi-angle laser light scattering detection.
SEM	scanning electron microscopy.
TPBVP	two point boundary value problem.

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