Macromol. Symp. 2009, 283–284, 103–109

DOI: 10.1002/masy.200950914

Evaluation of the Performance of a Kinetic Model for Free-Radical Copolymerization of Vinyl/Divinyl Monomers in Supercritical Carbon Dioxide

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Summary: The performance of a mathematical model for free radical copolymerization kinetics with crosslinking of vinyl/divinyl monomers in supercritical carbon dioxide previously developed in our group is evaluated using experimental data of conversion versus time and gel fraction versus conversion for copolymerization of styrene and divinylbenzene. The effects of process conditions, type of stabilizer and initial divinyl monomer composition were also assessed. Reasonable agreement between model predictions and experimental data was obtained.

Keywords: copolymerization; crosslinking; modelling; polymerization kinetics; supercritical carbon dioxide

Introduction

Supercritical carbon dioxide ($scCO_2$) is an atractive medium for polymerization processes because of its its low toxicity, mild critical point ($T_c = 31.1\,°C$, $P_c = 73.8$ bar) and enviromentally friendly nature.[1,2] Supercritical fluids can exhibit the best of two worlds: they can have gaslike diffusivities and liquidlike densities. In the vicinity of the fluid's critical point, its density is highly sensitive to modest changes in pressure and temperature.

Many polymers have been synthesized in $scCO_2$, including fluoropolymers, polysiloxanes, polymethyl methacrylate (PMMA), polystyrene (PS) and polycarbonates, as reviewed elsewhere.[3–6] Most of the polymeric material obtained in $scCO_2$ are produced by heterogeneous process.[7–16]

Crosslinked polymers (polymer networks) are important in many technological applications including medicine, biotechnology, agriculture, and other areas. They are used as construction materials, paints and coatings, polymer glasses with high mechanical strength and high thermal stability, rubbers, ion-exchange resins and sorbents, insoluble polymer supported reagents, controlled drug-release matrices, electronics and cabling, food packaging, sensors, "smart" materials, artificial organs, implants, and superabsorbent materials.[17,18]

Poly(styrene-co-divinylbenzene) is a crosslinked polymer used for chromatographic applications and as precursor for ion-exchange resins, among other uses. It is also a model system in the study of network formation via crosslinking free-radical copolymerization. The experimental study of commercial divinylbenzene (a mixture of meta- and para- isomers of divinylbenzene, ethylvinyl benzene, and other minor impurities) dispersion copolymerization in carbon dioxide at supercritical conditions has already been addressed by Cooper et al.[19,20] Also, in our group we carried out an experimental kinetic study for the copolymerization of styrene/divinylbenzene at several process conditions.[21]

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To the best of our knowledge, the first paper where the modeling of a heterogeneous free-radical copolymerization in $scCO_2$ is reported, was presented by our group in 2005.[22] Our kinetic model can predict overall conversion, copolymer composition, molecular weight development, appearance of the gel point, and evolution of gel fraction and average crosslink density.

The objective of this work is to experimentally validate our 2005 model[22] by contrasting experimental data of overall conversion and gel fraction evolution, for the copolymerization of styrene and divinylbenzene (DVB) in $scCO_2$, using two different stabilizers.[21] The effect of polymerization conditions on overall monomer conversion, and gel fraction is analyzed.

Modeling

The chemical system to be analyzed in this paper is the free radical copolymerization with crosslinking of vinyl/divinyl monomers in $scCO_2$. The kinetic scheme can be treated as if it was a homopolymerization by making use of the ''pseudo-kinetic rate constants method'', developed by Hamielec and MacGregor[23]. The method of moments is used to monitor the molecular weight development. Initiation, propagation and termination reactions are considered to be diffusion-controlled, and are modelled using a free-volume theory from the beginning of the polymerization.

The free-radical polymerization at supercritical conditions proceeds as a heterogeneous process where dispersed particles are formed in the presence of an adequate stabilizer, with a homogeneous reaction mixture at the beginning of the polymerization. This process can be described as proceeding in three stages[24]. The partition of monomer between the two phases is modeled following the approach proposed by Kiparissides et al.[24] In that approach, the process is assumed to proceed in three stages. A description of the phenomena and species involved in each stage has been discussed elsewhere.[22] Here, only the resulting equations for each stage are shown; Equation (1)–(6), below.

Stage 1 ($0 < x < x_s$): This stage proceeds as a solution polymerization process, from the start of the polymerization until a limiting conversion, x_s (conversion where the polymer chains precipitate and form a second phase), which is associated to the polymer solubility, is reached.

$$G_{m_1} = G_{m_0}(1 - x) \tag{1}$$

$$G_{m_2} = 0 \tag{2}$$

Stage 2 ($x_s < x < x_c$): Two-phase polymerization. This stage lasts from the appearance of the second phase, until the monomer in the continuous phase is completely consumed.

$$G_{m_1} = G_{m_0}\left(1 - x - \frac{x}{x_c(1+K)} + \frac{x}{1+K}\right) \tag{3}$$

$$G_{m_2} = G_{m_0}x\left(\frac{\frac{1}{x_C} - 1}{1+K}\right) \tag{4}$$

x_c is defined as a critical conversion where all the monomer is in the disperse phase. K in Equation (3)–(4) is defined as the ratio of mass of CO_2 to mass of monomer, in the dispersed phase.[24]

Stage 3 ($x_c < x < 1$): The polymerization proceeds only in the dispersed phase. The amount of total polymer in the continuous and dispersed phases, during stage 3, is now given by Equation (5)–(6).

$$G_{m_1} = 0 \tag{5}$$

$$G_{m_2} = G_{m_0}(1 - x) \tag{6}$$

It was assumed[22] that the ratio of initiator concentration to total monomer concentration is the same for both phases, at any given time, which leads to Equation (7)–(8).

$$[I]_1 = \frac{[I]}{\frac{[M]_2}{[M]_1} + 1} \tag{7}$$

$$[I]_2 = [I] - [I]_1 \tag{8}$$

More details about the model can be found in Quintero-Ortega et al.[22]

Results and Discussion

The system analyzed was the copolymerization of styrene and DVB in supercritical carbon dioxide. Four cases (Cases 1–4) studied experimentally by García-Morán et al.[21] were simulated. In the first one, experimental conditions were carried out at 65 °C and 172 bar, and PSDMS (Polystyrene-block-polydimethylsiloxane) was used as stabilizer. The second one was polymerized at the same conditions, but using Krytox 257 FSL (DuPont) as the stabilizer. In the last two cases the stabilizer was PSDMS, and 70 °C and 241 bars were used in Case 3, and 80 °C and 310 bar for Case 4, respectively.

The model parameters were gathered from literature as shown in Table 1. The kinetic rate constants were corrected for pressure. All the parameters used in the simulation of Case 1 are summarized in Table 1. All the parameters used in the model are defined in the nomenclature section of this paper.

The agreement between model predictions and experimental data of conversion versus time for Case 1 is fairly good (see Figure 1). In five hours 80% of monomer has converted into polymer, and total monomer conversion is reached in less than 10 hours.

The polymerization conditions used in Case 2 are the same as in Case 1, except that

Table 1.
Kinetic and Physical Parameters for the copolymerization of Styrene and DVB at 65 °C and 172 bar using Krytox 257 FSL as stabilizer.

Parameter, units	Value	Reference
f_o, dimensionless	0.7	25
k_d, s^{-1}	1.6053×10^{-5}	22
k_{11}, L mol^{-1} s^{-1}	332.82	22
k_{22}, L mol^{-1} s^{-1}	$\left(\frac{k_{22}}{k_{11}}\right)_m = 0.95,\ \left(\frac{k_{22}}{k_{11}}\right)_p = 1.9$	25
k_{fp}, L mol^{-1} s^{-1}	0.0	25
k_{tc}, L mol^{-1} s^{-1}	1.2841×10^{8}	22
k_{td}, L mol^{-1} s^{-1}	2.073×10^{-13}	25
k_{ft1},k_{ft2}, L mol^{-1} s^{-1}	0.0133 k_{11}	25
k_{ft3}, L mol^{-1} s^{-1}	2 k_{11}	25
$(r_1)_m$, dimensionless	$\left(\frac{k_{11}}{k_{12}}\right)_m = 0.4$	25
$(r_2)_m$, dimensionless	$\left(\frac{k_{22}}{k_{21}}\right)_m = 1.0$	25
$(r_1)_p$, dimensionless	$\left(\frac{k_{11}}{k_{12}}\right)_p = 0.13$	25
$(r_2)_p$, dimensionless	$\left(\frac{k_{22}}{k_{21}}\right)_p = 2.0$	25
$(r_1)_{mix}$, $(r_2)_{mix}$, dimensionless	$(r_i)_{mix} = \frac{\left[n_p (r_i)_p + n_m (r_i)_m\right]}{n_p + n_m}$	25
k_{31}, L mol^{-1} s^{-1}	$(k_{31})_m = 0.0067 k_{11},\ (k_{31})_p = 0.109 k_{11}$	25
k_{32}, L mol^{-1} s^{-1}	$\left(\frac{k_{32}}{k_{31}}\right) = r_2$	25
k^*_{3i}, L mol^{-1} s^{-1}	$\left(\frac{k^*_{3i}}{k_{11}}\right)_m = 2\left(\frac{k^*_{3i}}{k_{11}}\right)_p,\ \left(\frac{k^*_{3i}}{k_{11}}\right)_p = 0.626 + \frac{1.245*10^{-3}}{f_{20}}$	25
k^*_{3i}, L mol^{-1} s^{-1}	$\left(k^*_{3i}\right)_{mix} = \frac{\left[n_p \left(k^*_{3i}\right)_p + n_m \left(k^*_{3i}\right)_m\right]}{n_p + n_m}$	25
k_{cp}, dimensionless	0.25	25
k_{cs}, dimensionless	0.0	25
$D_1 = D_2$, dimensionless	0.001	25
A_1, dimensionless	0.0	22
A_2, dimensionless	0.465	22
x_s, dimensionless	0.043	22
x_c, dimensionless	0.4	22
K, ratio of mass of solvent to mass of monomer, in the dispersed phase	0.00881	22

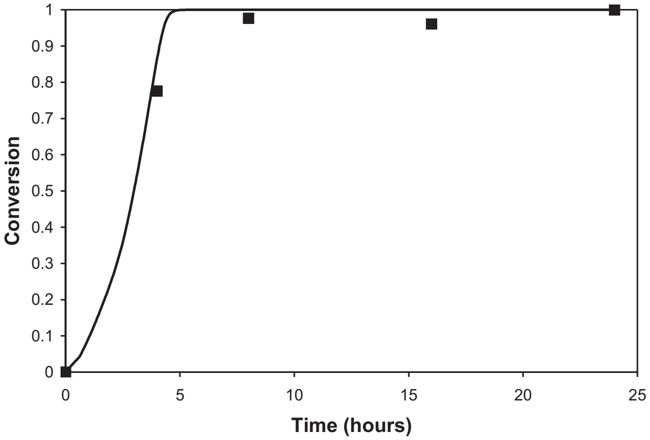

Figure 1.
Conversion versus Time for the Copolymerization of Styrene and DVB at 65 °C and 172 bars, using Krytox 257 FSL as stabilizer.

in Case 2 the stabilizer used is PSDMS, and not Krytox 257 FSL. It is observed in Figure 2 that much lower conversions (slower polymerization rate) are obtained with PSDMS. García-Morán et al.[21] reported that partial agglomeration of particles was always present in their experiments when PSDMS was used as stabilizer. Therefore, Krytox 257 FSL was more effective as stabilizer than PSDMS for copolymerization of STY/DVB in $scCO_2$. Since the only difference between Cases 1 and 2 was the stabilizer used, the only model parameters that could be different where those related to the partition of components between the two phases (x_s, x_c, and K). These parameters were fine-tuned using the experimental data corresponding to Case 2. The adjusted parameters are reported in Table 2.

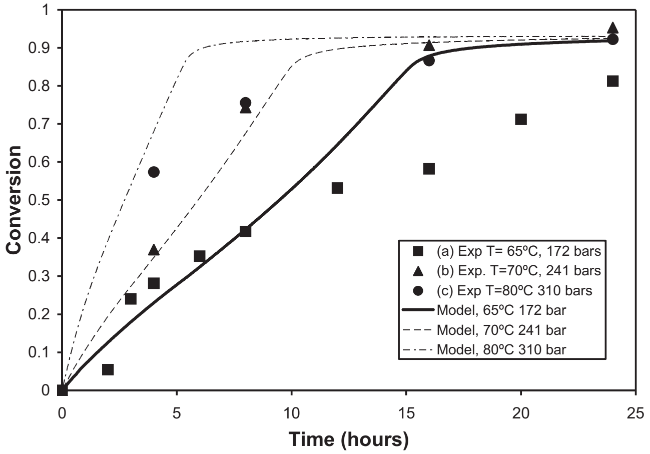

Figure 2.
Conversion vs time Copolymerization for Styrene and DVB at the conditions indicated by the symbols, with PSDMS as stabilizer.

Table 2.
Physical Parameters for the copolymerization of Styrene and DVB.

Parameter, units	Case 2	Case 3	Case 4	Reference
f_o, dimensionless	0.7	0.7	0.7	22
k_d, s^{-1}	1.6053×10^{-5}	3.1165×10^{-5}	1.0929×10^{-4}	22
k_{11}, L mol^{-1} s^{-1}	332.82	399.95	568.81	22
k_{tc}, L mol^{-1} s^{-1}	1.2841×10^{8}	1.4383×10^{8}	1.8616×10^{8}	22
x_s, dimensionless	0.043	0.043	0.043	22
x_c, dimensionless	0.3	0.3	0.3	See text
K, dimensionless	3.0	3.0	3.0	See text
vcr2, dimensionless	0.1	0.1	0.1	See text
Initial initiator concentration	0.0135	0.0135	0.0135	21
Initial Monomer concentration	2.047	2.04	2.052	21
Initial DVB mol fraction	0.1568	0.159	0.158	21
Solvent concentration	10.66	12.16	12.668	21

Figure 2 shows a comparison of model predictions and experimental data of conversion versus time for the three cases using PSDMS as stabilizer. It is observed that the agreement is not as good as with the case with Krytox 257 FSL. The conversion versus time profile obtained with the model is close to the experimental data up until 8 hours (approximate 40% monomer conversion). At higher conversions the predicted profiles significantly deviate from the experimental data. It may be possible that diffusion-controlled propagation (neglected in the calculations) could become important in the agglomerated clusters produced in the high pressure view-cell used as reactor. If temperature and pressure are increased, then polymerization proceeds faster. The value of K was varied from 0.00881 to 3.0 because we assumed that the polymer network capture significant amounts of supercritical carbon dioxide, which swells the polymer network. That is why the value of K can become higher than one. It was also assumed that the monomer migrates faster to the polymer drops (the polymerization occurs inside the drops, mainly). That causes the critical monomer conversion, x_c, being lower. Given the fact that both monomers

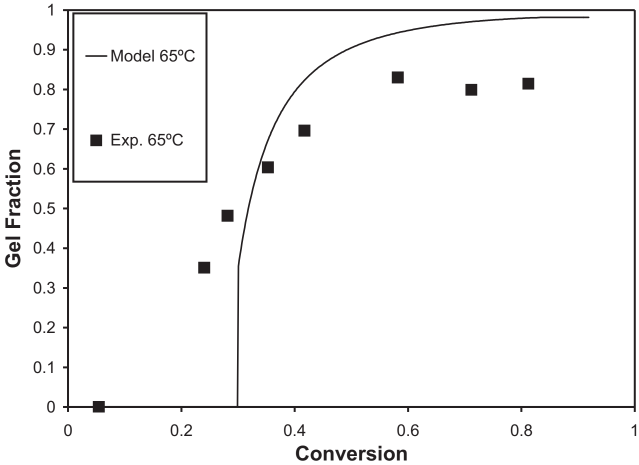

Figure 3.
Gel Fraction evolution for the copolymerization of Styrene and DVB at 65 °C and 172 bars using PSDMS as stabilizer.

are soluble in $scCO_2$, it would be expected that x_c should be equal to 1.0, namely, that there should be monomer in the continuous phase during all the polymerization. This result may also suggest an inadequacy of the model.

Figure 3 shows the gel fraction evolution for the copolymerization of STY/DVB in $scCO_2$ at 65 °C and 172 bars, using PSDMS as stabilizer. The agreement between the predicted and experimental profiles is reasonably good.

Conclusions

Although the model used for calculation of the partition of components between the two phases has some limitations, as pointed out by Quintero-Ortega et al.,[22] the agreement obtained between model predictions based on it and experimental data from García-Morán et al.[21] is reasonably good. The model captures all the features of the copolymerization, but the quantitative agreement is only moderately acceptable.

Nomenclature

A_1	Effectiveness factor to account for overlap of free volume and separation of reactive radicals in phase 1
A_2	Effectiveness factor to account for overlap of free volume and separation of reactive radicals in phase 2
D_1	Effectiveness factor to account for overlap of free volume and separation of fragment radical molecules in phase 1
D_2	Effectiveness factor to account for overlap of free volume and separation of fragment radical molecules in phase 2
f_0	Initiator efficiency
Gm_0	Initial mass of monomer, g.
Gm_1	Mass of monomer 1, g.
Gm_2	Mass of monomer 2, g.
$[I]$	Initiator concentration, mol^*L^{-1}
$[I]_0$	Initial initiator concentration, mol^*L^{-1}
$[I]_1$	Initiator concentration in phase 1, mol^*L^{-1}
$[I]_2$	Initiator concentration in phase 2, mol^*L^{-1}
K	Solubility constant of monomer in solvent.
k_{cp}	Proportionality constant between primary cyclization density and mole fraction of divinyl monomer bound in the polymer chains
k_{cs}	Proportionality constant between the average number of secondary cycles per crosslinking and the fraction of free pendant double bonds in the primary polymer molecule
$k_{d,j}$	Initiator decomposition kinetic constant, s^{-1}
$k_{fp,j}$	Pseudo-kinetic constant for chain transfer to polymer, $l^*mol^{-1*}s^{-1}$
$k_{fT,j}$	Pseudo-kinetic constant for chain transfer to a small molecule, $l^*mol^{-1*}s^{-1}$
$k_{i,j}$	Pseudo-kinetic constant for propagation, $l^*mol^{-1*}s^{-1}$
k^*_j	Pseudo-kinetic constant for propagation through pendant double bonds, $l^*mol^{-1*}s^{-1}$
$k_{tc,j}$	Pseudo kinetic constant for termination by combination in phase j, $l^*mol^{-1*}s^{-1}$
$k_{td,j}$	Pseudo kinetic rate constant for termination by disproportionation, in phase j, $l^*mol^{-1*}s^{-1}$
$[M]_1$	Concentration of monomer in phase 1
$[M]_2$	Concentration of monomer in phase 2
P_c	Critical Pressure
r_1	Reactivity ratio
r_2	Reactivity ratio
T_c	Critical Temperature
V_{fcr2}	Critical fractional free volume for glassy effect
x	General (overall) conversion
x_c	Critical conversion
x_S	Limit solubility conversion

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