HIGH TEMPERATURE FREE-RADICAL COPOLYMERIZATION OF STYRENE AND METHYL METHACRYLATE IN SOLUTION WITH scCO₂

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ABSTRACT

High-temperature styrene-methyl methacrylate copolymerizations in solution with 20 wt% scCO₂ yielding low molecular weight polymers ($M_n \sim 2500$ g·mol^{-1}) were investigated and modeled considering the effect of depropagation. The simulations were carried out using the simulation package PREDICI®. Since the targeted polymer have chain lengths well below 100, the influence of chain-length-dependent termination kinetics is considered for modeling. Additional phase-behavior calculations showed that the solution remains single-phase throughout the reaction.

INTRODUCTION

Traditional solvent-borne acrylic resins consisting of high-molecular-weight polymers that are produced at low temperatures (< 80 ºC) need high levels of organic solvent (70 %) to be processed as coatings. Alternatively, novel resin compositions consist of acrylic oligomers with multiple functional groups that can undergo crosslinking reactions on the substrate surface. Frequently, styrene-methacrylate copolymers are used as binder resins in automotive coatings.

Supercritical (sc) CO₂ turned out to be an attractive solvent for a wide variety of chemical processes. Besides being environmentally friendly, interesting features of using scCO₂ in polymerizations are associated with the lowering of viscosity and with the ease, by which polymer may be separated from the product mixture. In addition, scCO₂ may be used in polymer processing, e.g. for impregnation or particle formation [1]. Most common polymers exhibit poor solubility in scCO₂. Thus, polymerizations of conventional monomers were mostly carried out in heterogeneous phase [2]. However, it was shown that homogeneous-phase copolymerizations may be carried out, as long as rather low-molecular-weight polymers were obtained and rather low CO₂ contents of 20 wt% were used [3,4]. With respect to process intensification it seems rewarding to carry out radical polymerizations at elevated temperatures (>120 °C). The benefits of higher temperatures are plentiful, e.g., use of initiators with low SADT (self accelerating decomposition temperature), reduction in initiator concentrations and a positive influence on continuous processes due to lowering viscosity. The drawback of this method is that these high temperature and solution polymerization conditions promote secondary reactions, e. g., such as methacrylate depropagation, that affect propagation rate, degree of monomer conversion, and molecular weight of the final product.

Modeling of these polymerizations is of eminent importance, because polymerization rate and polymer architecture strongly depend on the reaction conditions. In particular polymerizations in scCO₂ need to be accompanied by modeling, since the phase behavior of

the reaction mixture at a given temperature and pressure is affected by polymer molecular weights. Since polymerizations carried out in the presence of scCO$_2$ are experimentally and time demanding, modeling of the polymerizations is thus highly recommendable to reduce the number of experiments required. As in any other radical polymerization, reaction kinetics and polymer properties are closely related. Thus, the knowledge of reliable kinetic coefficients is essential for modeling polymerizations.

MATERIALS AND METHODS

The monomers styrene (STY, 99 %, Merck-Schuchardt) and methyl methacrylate (MMA, 99 %, stabilized with 0.02 wt % hydroquinone, Fluka) were purified with an inhibitor remover (Aldrich Chemie) and subsequently distilled under reduced pressure. The initiator di-*tert*-butyl peroxide (DTBP; kindly provided by AKZO Nobel) and carbon dioxide (CO$_2$; grade 4.5, Messer Griesheim) were used as received. The reaction mixture containing 20 wt% CO$_2$, 3.3 wt% DTBP and a styrene content of f_{STY} = 0.07 in the monomer feed was prepared as previously detailed [2]. The polymerizations were performed at 170 °C and 350 bar in batch after rapidly introducing the premixed homogeneous reaction mixture into the preheated optical high-pressure cell. Due to the small reaction volume of 0.8 mL, the polymerization mixture reaches the reaction temperature almost instantaneously. The monomer concentration was monitored throughout the reaction via quantitative Fourier-Transform near infrared (NIR) spectroscopy in the region of the first overtones of the C-H stretching modes around 6171 cm^{-1} [5]. Molecular weight distributions were determined by size-exclusion chromatography (SEC) as detailed in Ref. [3].

KINETIC MODEL AND RATE COEFFICIENTS

The kinetic model includes chemical initiation, thermal initiation of monomers, propagation according to the penultimate unit model, depropagation, and termination as shown in Table 1. Transfer events to monomer and polymer were neglected, because rather high initiator concentrations were applied to allow for effective molecular weight control via initiation rate. Depropagation only occurs with methacrylate units in both the penultimate and terminal positions of the polymer radicals [6]. P_{ij} represents the probability of having a penultimate unit i attached to the terminal radical j. P_{ij} is calculated as detailed in Ref. [6, 7].

Table 1:

kinetic mechanisms of high-temperature methyl methacrylate (1)/styrene (2) copolymerization

Initiation	$I \xrightarrow{k_d} 2fI^{\bullet}$
	$I^{\bullet} + M_k \xrightarrow{k_{pkkk}} P_1^{k\bullet}$
MMA thermal initiation	$M_1 + M_1 \xrightarrow{k_{pthm}} P_2^{1\bullet}$
Styrene self-initiation	$2M_2 \xrightarrow{k_1} DA$
	$DA \xrightarrow{k_{-1}} 2M_2$
	$DA + M_2 \xrightarrow{k_i} P_1^{2\bullet} + P_2^{2\bullet}$
Propagation	$P_n^{j\bullet} + M_k \xrightarrow{P_{ij}k_{ijk}} P_{n+1}^{k\bullet}$
Termination	
by combination:	$P_n^{j\bullet} + P_n^{k\bullet} \xrightarrow{<k_{tcjk}>} D_{n+r}$
by disproportination:	$P_n^{j\bullet} + P_n^{k\bullet} \xrightarrow{<k_{tdjk}>} D_n + D_r$
Depropagation	$P_{n+1}^{1\bullet} \xrightarrow{P_{11}k_{dep}} P_n^{1\bullet} + M_1$

The decomposition rate coefficients, k_d, and the initiator efficiencies, f, were adopted from literature [8]. The initiator efficiency f was considered to be independent of monomer conversion, because the targeted polymer molecular weights are low. The rate coefficients k_{pMMM} and k_{pSSS} may be calculated from the Arrhenius parameters and activation volumes reported for bulk polymerizations. The use of bulk data is appropriate since it was shown that styrene is not influenced by the presence of CO$_2$ and since MMA is only affected by CO$_2$ for reactions leading to high MW material [9].

The monomer and radical reactivity ratios were taken from literature [10, 11]. For MMA, the depropagation rate coefficient k_{dep} was estimated by comparing modeled and experimentally derived monomer conversions [12]. The notation $<k_t>$ indicates a chain-length averaged mean value of the termination rate coefficient; $<k_t> = <k_{tc}> + <k_{td}>$, where $<k_{tc}>$ accounts for termination via combination and $<k_{td}>$ for termination via disproportionation. $<k_{t,STY}>$ was taken from literature [9, 14], while the MMA value was estimated by comparison of modeled and experimentally derived monomer conversions and molecular weight distributions (MWD). The simplified model expression for $<k_{t,copo}>$, as suggested by Buback et al. [13], has been adopted.

CHAIN LENGTH DEPENDENT (CLD) TERMINATION

The termination rate coefficient k_t is influenced by a multitude of different factors. All parameters that can exert an effect on the mobility of radicals will have an effect on the overall termination rate coefficient. As large coils are known to diffuse less rapidly than small ones, the radical chain length has a profound effect on the termination kinetics. Therefore, a single rate coefficient k_t cannot describe all termination events occurring in a polymerizing system at any instant, because radicals of a variety of sizes are present. Thus, one must properly describe termination in terms of $k_t(i, j)$, the rate coefficient for termination between radicals of chain lengths i and j respectively. In carrying out a free-radical polymerization experiment, one will invariably measure the overall rate of termination, which is the sum of the rates of termination for all possible pairs of radical sizes.

To account for chain-length dependent termination, it was suggested to use a "composite model" [15], which distinguishes short and long radicals.

$$k_t(i,j) = k_t^0 \cdot i_c^{-\alpha_1} \tag{1}$$

$$k_t(i,j) = k_t^0 \cdot i_c^{-\alpha_1+\alpha_2} \cdot i^{-\alpha_2} \tag{2}$$

$$k_t(GM) = \sqrt{k_t^{i,i} \cdot k_t^{j,j}} \tag{3}$$

In Eqs. (1) and (2), α_1 refers to "short" and α_2 to "long" radicals. k_t^0 is the rate coefficient for termination between two monomeric radicals. GM indicates that a geometric mean value for $k_t^{i,j}$ is considered. Smith et al. [16] successfully applied this composite model to MMA homopolymerization modeling and found that the GM model for cross termination is computationally less demanding but at the same time reliably reproduces the general trends. The α_2 value of ~ 0.16 is applied for the treatment of chain lengths above ~ 100. For shorter chains, $\alpha_1 = 0.5$ is used. Recently, the occurrence of two such α values for short and long radicals was also shown experimentally [17, 18]. Thus, modeling of polymerizations may require a composite model to account for the chain-length dependence of k_t. With respect to the copolymerizations considered in this work, the majority of radicals will have a chain length below 100. With $\alpha_1 = 0.5$, a decrease in $k_t^{i,i}$ by one order of magnitude occurs in going from $i = 1$ to $i = 100$. The values of k_t^0 for each of the monomers were assumed to be equal and were estimated by comparing modeled and experimentally derived monomer conversions.

PHASE BEHAVIOR

For the component i to be in homogeneous solution with a mixture requires

$$(\mu_i^0 - \mu_i)\Big/RT > 0 \tag{4}$$

Where μ_i^0 is the chemical potential of component i in the pure state, μ_i is the chemical

potential of component i in the mixture. For monomer and solvent the chemical potentials have been computed in the frame of the Sanchez-Lacombe model as follows.

$$\frac{\mu_i}{RT} = \ln\phi_i + (1 - \frac{r_i}{r}) + r_i\tilde{\rho}\left(\sum_{j=1}^{n}\phi_i\chi_{ij} - \sum_{j=1}^{n}\sum_{k=j+1}^{n}\phi_j\phi_k\chi_{jk}\right) + r_i\left[-\frac{\tilde{\rho}}{\tilde{T}_i} + \frac{\tilde{P}_i}{\tilde{T}_i\tilde{\rho}} + \left(\frac{1}{\tilde{\rho}} - 1\right)\ln(1-\tilde{\rho}) + \frac{1}{r_i}\ln\tilde{\rho}\right] \quad (5)$$

Where n, the component number, is equal to 2 (CO_2 and monomer) and 3 (CO_2, monomer and polymer) in the mixture. Full details about all variables in this equation can be found in the original papers of Sanchez et al. [19, 20]. In Eq. (5) ρ refers to the molar density of the mixture, P is the pressure and T the temperature. The molar density of the mixture may be computed from the Sanchez-Lacombe equation of state in reduced form:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left[\ln(1-\tilde{\rho}) + \left(1 - \frac{1}{r}\right)\tilde{\rho}\right] = 0 \quad (6)$$

Where the following definitions apply to the reduced variables:

$$\tilde{\rho} = \frac{\rho r v^*}{M_m} \quad \tilde{P} = \frac{Pv^*}{\varepsilon^*} \quad \tilde{T} = \frac{TR}{\varepsilon^*} \quad (7)$$

r, v^*, and ε^* being three characteristic parameters, M_m is the mixture molecular weight and R is the ideal gas constant. While for the pure components the characteristic parameters are usually known, for the mixture they are evaluated through mixing rules [20]. In the case of a copolymerization, comonomer and copolymer component parameters are estimated using the method of Panayiotou [21]. The interaction parameters, $\xi_{CO2\text{-}monomer}$ and $\xi_{\text{-}monomer\text{-}polymer}$ are taken from the work of Mueller et al. [22], while $\xi_{CO2\text{-}polymer}$ is taken from Liu et al. [23] and are assumed to be valid for copolymerizations.

The equation of state is applied to the mixture and, in combination with the constraint of a constant reactor volume, allows for computing overall pressure.

RESULTS
Two models, A and B, were studied. They refer to the experimental run described earlier. Model A ignores CLD of k_t whereas B accounts for CLD k_t. Monomer consumption during polymerization results in an increase in the density of the mixture, associated with a substantial decrease in pressure, as is shown in Fig 1. Pressure changes during polymerization which is not surprising, since the molar volume of a vinyl monomer is higher than the one of the corresponding polymer. The stability criterion calculated for component CO_2 is shown in Fig. 2. For both models, it is seen that throughout the reaction the solution remains in single phase. Figs. 3 and 4 show experimental and modeled conversion $vs.$ time curves and MWDs, respectively. Both models (no CLD of k_t and CLD of k_t being considered) predict almost identical conversion $vs.$ time profiles. The agreement between calculated and experimental data is satisfactory. The low-MW material detected experimentally and via modeling originates from termination of radicals consisting of one initiator fragment and one or two monomer units with each other or with an initiator fragment. It is evident that the modeling results do not show such a clear structure of the MWD in the low MW region (see Fig. 4). This is mainly due to the modeling algorithm. Recently, Monte Carlo simulations were successfully used to capture low molecular weight species in RAFT polymerizations [24]. In addition, at the high temperature of 170 °C upon depressurization of the reaction mixture, low molecular weight oligomers may be lost. It is seen that modeling with CLD termination kinetics provides better match of experimental data compared to modeling with ignoring CLD of k_t.
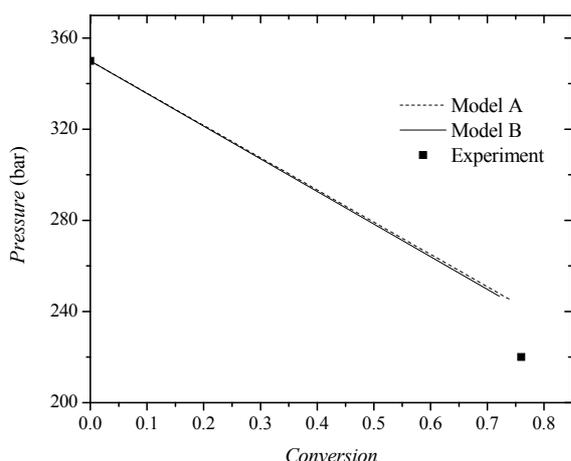
Fig 1: Pressure as a function of conversion.
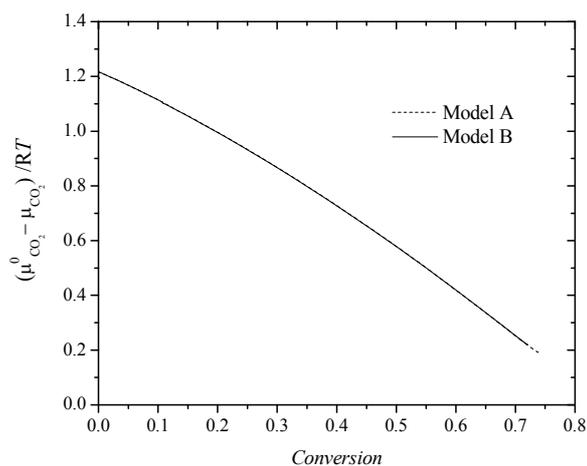
Fig 2: Stability criterion as a function of conversion.
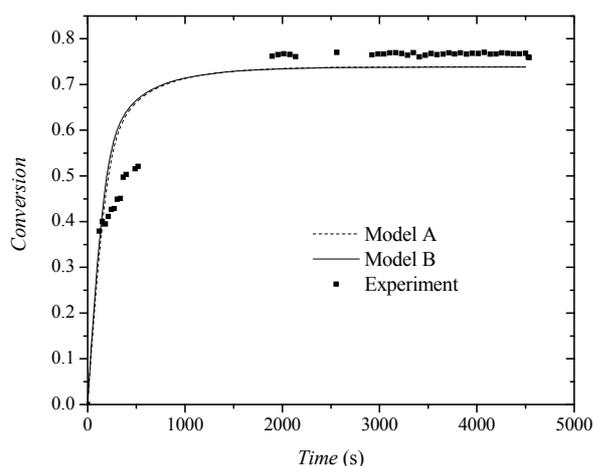
Fig 3: Experimental and modeled conversion as a function of time.
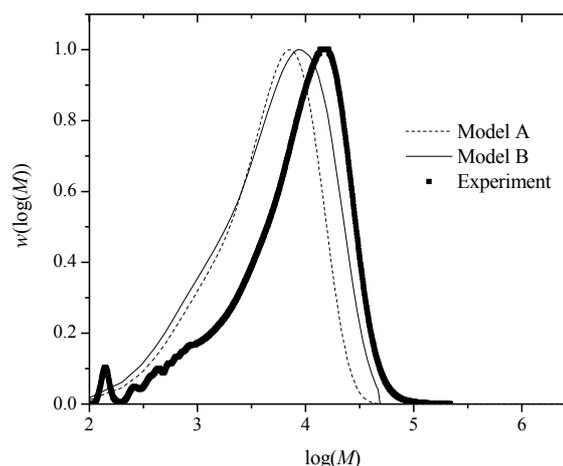
Fig 4: Experimental and modeled MWDs.

CONCLUSIONS:

The modeling of high-temperature free-radical STY-MMA copolymerization in solution with 20 wt% CO_2 was addressed. A mechanistic kinetic model provides a good representation of the experimental observations, after fitting depropagation and termination rate coefficients to the experimental data. Incorporation of chain-length-dependent termination in the modeling allows for a better match of experimental and modeled MWDs.

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