Pressure and Temperature Dependence of the Propagation Rate Coefficient of Free-Radical Styrene Polymerization in Supercritical Carbon Dioxide

Sabine Beuermann,*,† Michael Buback,† Christoph Isemer,† Igor Lacík,‡ and Almut Wahl†

Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Tammannstr. 6, 37077 Göttingen, Germany, and Polymer Institute of the Slovak Academy of Sciences, Dubravska Cesta, 84236 Bratislava, Slovak Republic

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ABSTRACT: Free-radical polymerization of styrene in homogeneous phase of supercritical carbon dioxide ($scCO_2$) has been studied at temperatures between 40 and 80 °C and pressures between 300 and 1500 bar. Applying pulsed-laser polymerization in conjunction with size-exclusion chromatography yields propagation rate coefficients, k_p. Within the extended pressure range under investigation, k_p for solution polymerization in carbon dioxide, at CO_2 contents up to 46 wt %, is identical to k_p of styrene bulk polymerizations. The studies with CO_2 suggest that solvent effects on k_p occur in systems where the solvent quality for the polymer is not very high *and* where *intra*segmental interactions are important.

Introduction

Supercritical carbon dioxide ($scCO_2$) has been demonstrated to be a promising alternate solvent medium for free-radical polymerizations.[1] Most studies focused on polymer synthesis whereas kinetic data for polymerization in $scCO_2$ are still scarce, although rate coefficients are required for modeling and optimization of fluid-phase polymerizations. Investigations into methyl methacrylate (MMA) and butyl acrylate (BA) polymerizations in solution of $scCO_2$ showed that the propagation rate coefficients, k_p, are below the corresponding bulk values.[2,3] On the other hand, a study into MMA solution polymerization in $scCO_2$ where polymer molecular weight was kept low showed no influence of CO_2 content on k_p.[4] Further, in styrene polymerizations carried out at 65 °C and 180 bar yielding low molecular weight polymer, no influence of CO_2 on k_p was detected.[4] Recently, it was demonstrated that the propagation kinetics of vinyl acetate homopolymerizations are not changed by the presence of CO_2.[5] These findings for polymerizations in CO_2 were explained by differences in solvent quality of CO_2 for the polymers and by a competition of polymer solvation by the monomer and by the monomer/CO_2 mixture. Thus, it appeared interesting to extend the investigations to a system in which the solvent quality of CO_2 for the polymer is poor. Since polystyrene is considered to be the archetype of such a polymer with almost no solubility in CO_2,[6] the knowledge of k_p from styrene polymerizations in the presence of $scCO_2$ should contribute to a better understanding of solvent effects on k_p. Being aware of the findings for MMA polymerizations in CO_2, styrene experiments should be carried out such that high molecular weight material is produced.

The present paper reports propagation rate coefficients of styrene solution polymerization in $scCO_2$ determined via PLP−SEC (pulsed laser polymerization−size-exclusion chromatography). This technique is recommended by the IUPAC Working Party on “Modeling of Polymerisation Kinetics and Processes” as the method of choice for reliable k_p measurement.[7] Equally spaced laser pulses are applied to obtain polymer which is analyzed by SEC. Equation 1 is used for estimating k_p:

$$L_i = i k_p c_M t_d \qquad i = 1, 2, 3, ... \tag{1}$$

where L_i is the number of propagation steps between i successive laser pulses, t_d is the dark time between two laser pulses given by the inverse of laser pulse repetition rate, and c_M is monomer concentration. L_i is obtained as the degree of polymerization at the ith point of inflection (POI) of the molecular weight distribution (MWD). The POIs are directly determined from maxima of the first derivative curve of the experimental MWD.

Experimental Section

Styrene (Merck-Schuchardt, 99%) was washed with aqueous NaOH and with water to remove the inhibitor, then dried with Na_2SO_4, and distilled under reduced pressure. The photoinitiator for the PLP−SEC experiments, 2,2-dimethoxy-2-phenylacetophenone (DMPA, Aldrich-Chemie, 99%), was used without further purification. Carbon dioxide (CO_2, Messer Griesheim, grade 4.5) was used as received.

The experimental setup for preparation of the monomer−CO_2 mixture has already been detailed.[2] The initial homogeneous monomer−CO_2 mixture is fed into an optical high-pressure cell, which is subsequently disconnected from the pressure branch and inserted into the sample compartment of a FT-IR/NIR spectrometer (IFS 88, Bruker, Karlsruhe, F.R.G.). IR/NIR spectra are recorded using a tungsten halogen lamp, a silicon-coated CaF_2 beam splitter, and a liquid nitrogen-cooled InSb detector.

Initial styrene concentration, c_M^0, and monomer conversion during polymerization are determined via quantitative online NIR spectroscopy in the region of the first overtone of C−H stretching modes.[2] The monomer concentration c_M is calculated according to eq 2:

$$I_A = B c_M l \tag{2}$$

where I_A is the integrated absorbance and l is the optical path length. The integrated molar absorptivity, B, is available as a function of temperature and pressure from literature.[8] Contributions by CO_2 to the absorbance in the “styrene region”

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† Georg-August-Universität Göttingen.

‡ Polymer Institute of the Slovak Academy of Sciences.

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Table 1. Experimental Parameters and Results for PLP−SEC Experiments of Styrene in ScCO$_2$ at 80 °C and Different Pressures[a]

p/bar	c_M^0/ mol L^{-1}	c_{CO_2}/ wt %	ν/Hz	M_1/ g mol^{-1}	M_2/ g mol^{-1}	k_p/10^2 L mol^{-1} s^{-1}
300	4.63	41.2	10	34 500	69 200	7.15
300	4.54	42.3	10	32 000	65 400	6.77
500	5.09	39.9	10	38 400	73 000	7.23
1000	5.20	43.4	10	50 400	93 600	9.30
1500	5.18	43.8	10	62 300	119 000	11.6
1500	5.52	43.9	10	59 000	109 000	10.3
300	8.33	0	10	57 500	111 000	6.63
500	8.45	0	10	61 300	128 000	6.97
1000	8.74	0	10	79 400	162 000	8.73
1500	9.01	0	10	97 700	210 000	10.4

[a] p is pressure, c_M^0 the initial monomer concentration, c_{CO_2} the CO$_2$ concentration, n the laser pulse repetition rate, M_i (i = 1, 2) the molecular weight at the ith point of inflection, and k_p the propagation rate coefficient (calculated from M_1 via eq 1).

Table 2. Experimental Conditions and Results from Pulsed Laser-Induced Polymerizations of Styrene in scCO$_2$ at 300 bar and Different Temperatures[a]

T/°C	c_M^0/ mol L^{-1}	c_{CO_2}/ wt %	ν/Hz	M_1/ g mol^{-1}	M_2/ g mol^{-1}	k_p/10^2 L mol^{-1} s^{-1}
40	5.49	37.3	10	10 400	19 300	1.81
40	5.35	38.9	10	9 800	18 000	1.76
60	4.82	42.1	10	19 000	35 500	3.79
60	4.79	42.5	10	19 500	35 600	3.90
60	4.77	42.7	10	19 100	36 200	3.85
60	4.44	46.6	10	18 200	33 000	3.93
70	5.20	36.1	10	23 900	47 400	4.41
80	4.63	41.2	10	34 500	69 200	7.15
80	4.53	42.3	10	32 000	65 400	6.77

[a] Temperature T, initial monomer concentration c_M^0, CO$_2$ concentration c_{CO_2}, pulse repetition rate ν, molecular weight at the ith point of inflection M_i (i = 1, 2), and propagation rate coefficient k_p (calculated from M_1 via eq 1).

are eliminated by subtracting a weighted CO$_2$ calibration spectrum as described elsewhere.[2]

PLP−SEC experiments in the presence of CO$_2$ were carried out for c_M^0 ranging from 4.4 to 5.5 mol L^{-1}, which corresponds to about 40 wt % or 60 mol % CO$_2$. For comparison, also bulk styrene polymerizations were carried out. The reaction mixture was irradiated by sequences of laser pulses (using a LPX 210i laser operated on the XeF line at 351 nm, Lambda Physik) applied at repetition rates ν between 2 and 30 Hz, an energy of about 3 mJ per pulse, and a DMPA concentration of about 5×10^{-3} mol L^{-1}. Depending on temperature and pressure, between 3000 and 6000 pulses were applied to obtain styrene conversions between 1.5 and 3.5%. In all cases visual inspection of the inside of the optical high-pressure cell showed that the reaction mixture is homogeneous at these low degrees of monomer conversion typical for PLP−SEC experiments. Then, the system is depressurized by venting of the CO$_2$, and the polymer−monomer mixture is collected. The resulting polymer is precipitated with an excess of methanol (Fluka AG, p.a. grade) and is isolated. The polymerization conditions are summarized in Tables 1 and 2.

Molecular weight distributions were determined at 35 °C by SEC using a Waters 515 pump, a Waters 410 refractive index detector, and three PSS−SDV columns with nominal pore sizes of 10^5, 10^3, and 10^2 Å, respectively. Tetrahydrofuran (THF; Carl Roth, Rotipuran ≥99.5%, p.a.) was used at a flow rate of 1 mL/min as the eluent. Molecular weight calibration was established against narrow polydispersity polystyrene (PS) standards (MW = 410−2 000 000) from Polymer Standards Service (PSS, Mainz, F.R.G.).

Results

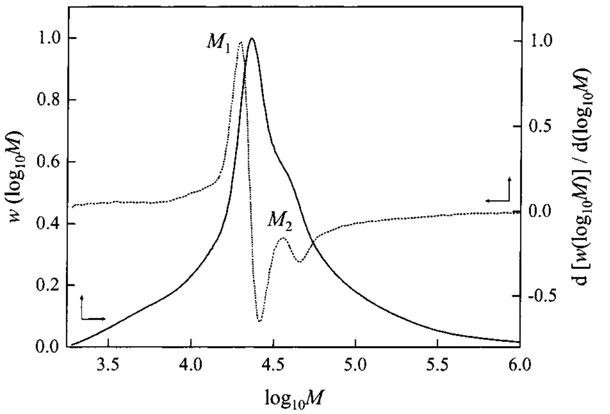

Figure 1. Molecular weight distribution (full line) and corresponding first-derivative plot (dashed line) of polystyrene obtained from a pulsed-laser styrene polymerization in scCO$_2$ at 60 °C, 300 bar, 42.5 wt % CO$_2$, and an initial monomer concentration of 4.79 mol L^{-1}.

The MWD of a polymer sample obtained from styrene PLP at 300 bar, 60 °C, a CO$_2$ content of 42.5 wt %, and a pulse repetition rate of 10 Hz is given by the solid line in Figure 1. The MWD shows a sharp peak at log M = 4.4 and a pronounced shoulder around log M = 4.6. The dashed line, which represents the first derivative of the MWD curve, exhibits two well-resolved maxima, corresponding to the first and second point of inflection, at log M_1 = 4.29 and log M_2 = 4.55. Dividing M_1 and M_2 by the molecular weight of the styrene repeat unit yields L_1 and L_2, respectively (see eq 1). The M_1 and M_2 values at the POI positions of each PLP experiment are summarized in Tables 1 and 2. The existence and the relative size, $M_2 \approx 2M_1$, serve as consistency criteria for reliable k_p determination via PLP−SEC.[7] The MWDs of polystyrene samples from polymerization at the lowest experimental temperature, 40 °C, and at 10 Hz even show a third and a weak fourth POI, L_1. The k_p values discussed within this study were exclusively obtained from the position of the first POI. A further important point to note is that the estimates of k_p from PLP−SEC are based on the assumption that the relevant monomer concentration, c_M, in eq 1 is given by the chosen (and in most cases also easily measurable) overall monomer concentration. As will be discussed further below, there may be monomer systems for which "local" monomer concentrations at the site of the free radical that differ from overall concentration.

Pressure Dependence of k_p. Propagation rate coefficients have been measured at 80 °C and various pressures, from 300 to 1500 bar. The CO$_2$ content was always close to 42 wt %. Table 1 contains the experimental parameters, the characteristic molecular weights M_1 and M_2 at the POIs, and the k_p value resulting from M_1 (or L_1).

Figure 2 shows the pressure dependence of k_p at 80 °C. The triangles are the data points for solution polymerizations in 42 wt % CO$_2$. The full line is fitted to these data. The dotted line represents the literature bulk k_p data.[9] The slopes of full and dotted lines are identical within experimental uncertainty. In absolute value, the solution (in CO$_2$) k_p data are, however, by about 10% below the bulk data from ref 9. This difference is within the accuracy of ±15% that is characteristic for k_p determinations via PLP−SEC.[7] As the performance of the SEC setup largely contributes to the reproducibility of PLP−SEC-derived k_p, a few additional PLP−SEC experiments for bulk styrene polymerizations at 80 °C have been carried out. The obtained polymer

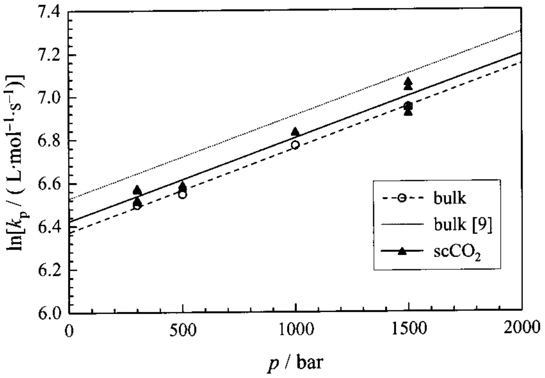

Figure 2. Pressure dependence of the propagation rate coefficient k_p for styrene polymerizations at 80 °C in scCO$_2$ (full triangles): open circles and dashed line, bulk k_p values from this work; dotted line, bulk k_p values from ref 9.

was analyzed on the same SEC instrument as were the PS samples from polymerization in CO$_2$. The resulting data points are given as open circles (Figure 2) with the fit to these data being represented by the dashed line. The results clearly show that, with the SEC analysis being carried out under the same instrumental conditions, no difference between styrene k_p data in bulk and in solution of CO$_2$ may be detected.

The pressure dependence of k_p for styrene polymerization in CO$_2$ (42 wt %) at 80 °C is given by eq 3:

$$\ln [k_p/(\text{L mol}^{-1}\,\text{s}^{-1})] = (6.42 \pm 0.04) + (3.84 \pm 0.39) \times 10^{-4}\,(p/\text{bar}) \quad (3)$$

$$(42 \text{ wt \% CO}_2,\ 80\ ^\circ\text{C},\ 300 \leq p \leq 1500 \text{ bar})$$

According to the general relation for the activation volume $\Delta V^{\#}$ associated with rate coefficient k: $\partial(\ln k)/\partial p = -\Delta V^{\#}/(RT)$, the activation volume of styrene k_p in CO$_2$ solution is obtained to be $\Delta V^{\#}(k_p, \text{scCO}_2) = -11.3 \pm 1.1$ cm^3 mol^{-1}. As is to be expected from Figure 2, this value is in close agreement with the corresponding value of styrene bulk polymerization: $\Delta V^{\#}(k_p, \text{bulk}) = -11.4 \pm 1.8$ cm^3 mol^{-1} (this work) and $\Delta V^{\#}(k_p, \text{bulk}) = -11.3 \pm 1.0$ cm^3 mol^{-1} reported in the literature.[9]

Temperature Dependence of k_p. The temperature dependence of k_p of styrene solution (in CO$_2$) polymerization was investigated between 40 and 80 °C at 300 bar. The CO$_2$ content was in the range from 36.1 to 46.6 wt % (see Table 2). The experimental k_p values are listed in the last column of Table 2 and are given as circles in the Arrhenius plot in Figure 3. The full line is fitted to this solution data whereas the dashed line represents the temperature dependence of bulk styrene k_p at 300 bar taken from the literature.[9] Again, the literature bulk k_p data is by about 10% above the solution data of the present investigation, which however is not indicative of any significant difference as has been discussed above. The k_p data thus is considered to be the same in bulk and in solution of CO$_2$. The solution data are fit by eq 4:

$$\ln [k_p/(\text{L mol}^{-1}\,\text{s}^{-1})] = (16.89 \pm 0.73) - (3661 \pm 250)(T^{-1}/\text{K}^{-1}) \quad (4)$$

$$(41 \text{ wt \% CO}_2,\ 300 \text{ bar},\ 40 \leq \Theta \leq 80\ ^\circ\text{C})$$

According to $\partial(\ln k)/\partial T^{-1} = -E_A/\text{R}$, the activation energy is obtained to be $E_A(k_p, \text{scCO}_2) = 30.4 \pm 2.1$ kJ mol^{-1} with this value being identical to the corresponding literature value for styrene bulk polymerization:[9] $E_A(k_p, \text{bulk}) = 30.7 \pm 3.2$ kJ mol^{-1}.

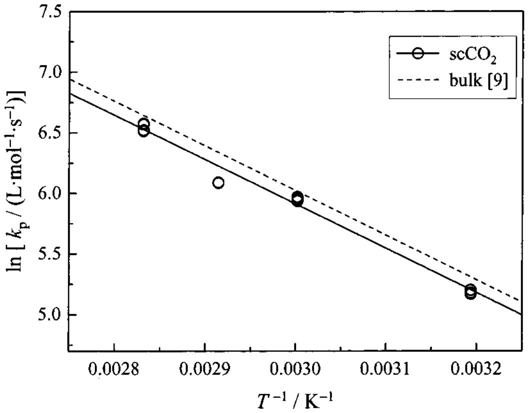

Figure 3. Arrhenius plot of the propagation rate coefficient, k_p, for styrene polymerizations at 300 bar in 40 wt % scCO$_2$ (open circles). The data for bulk polymerizations (dashed line) are taken from ref 9.

Discussion

A significant effect of fluid CO$_2$ on the propagation kinetics of butyl acrylate and methyl methacrylate free-radical polymerizations has recently been demonstrated.[2,3] Evaluation of PLP−SEC data obtained for these systems suggests a reduction in k_p upon the addition of CO$_2$ which reaches 40% at 40 wt % CO$_2$. As k_pc_M is the primary experimental quantity from PLP−SEC (see eq 1), it is however not clear whether the observed effect is entirely due to changes in either k_p or c_M or in both these quantities. The insensitivity of the kinetic parameters, $\Delta V^{\#}(k_p)$ and $E_A(k_p)$, toward the presence of CO$_2$ suggests that the reduction of k_pc_M in solution of CO$_2$ is essentially due to a lowering of “local” monomer concentration in the vicinity of the free-radical site. It is assumed that in going from bulk to solution in CO$_2$ experiments the balance of *intra*segmental interactions between the polar (meth)acrylate ester groups and of *inter*molecular segment−solvent interactions is shifted such that segment−monomer or segment−monomer/CO$_2$ interactions become less important and *intra*segmental interactions are favored. As a consequence of the poor solvent quality of CO$_2$ for polyacrylates, the effective “local” concentration of the acrylate monomer at the site of the free radical may be diminished.

One might anticipate an even more pronounced reduction in k_p for styrene polymerization in scCO$_2$, as polystyrene is known to be even less soluble in CO$_2$ than PBA and PMMA.[6] As can be seen from Figures 2 and 3, no such reduction is found. Styrene k_p is insensitive toward adding CO$_2$. This observation is however fully consistent with the explanation of a balance between *intra*segmental interactions and *inter*molecular segment−solvent interactions. As there will be no strong (polar) interactions between the phenyl groups, no reason is seen for a reduction in effective monomer concentration, and overall c_M should be a good measure of the “local” monomer concentration. Even if the overall monomer concentration differs from the local concentration, this difference should be the same for styrene polymerization in bulk and in solution of CO$_2$.

The k_p behavior of vinyl acetate polymerization in bulk and in solution of CO$_2$ provides further support for this line of arguments. Although polar *intra*segmental interactions must be expected to occur in vinyl acetate macroradicals, k_p of polymerizations in fluid CO_2 and in bulk are indistinguishable.[5] The reason for this type of behavior probably is the remarkably good solvent quality of $scCO_2$ for poly(vinyl acetate); e.g., the cloud point pressure at the temperatures of k_p experiments are by more than 1000 bar below the ones for the isomeric poly(methyl acrylate) even with the molecular weight of the latter material being lower.[6] The reason for the remarkably high solubility of poly(vinyl acetate) is not yet fully understood. The thermodynamic effect is however fully consistent with the kinetic observation made for k_p. Because of favorable *inter*molecular interactions with the CO_2-containing solvent medium, the balance of such *inter*molecular interactions with *intra*segmental interactions is rather similar in bulk and in solution (CO_2) polymerizations, and the overall concentration is representative of "local" concentration in the same way as with bulk polymerization. The observations made so far indicate an impact of thermodynamic effects of kinetic parameters. As the relative importance of *intra*- and *inter*molecular solvent action must be assumed to vary with temperature and pressure, the aspects of solvent-dependent propagation kinetics certainly should be addressed in even more detail and over wider ranges of p and T. It should be noted that it is due to CO_2 being such a special solvent that effects on propagation kinetics were detected. In situations where the solvent has similar solvent quality as has the monomer, k_p values calculated from eq 1 are not expected to be significantly different for bulk and solution polymerizations.[10] As there are indications of a chain length dependence of k_p,[11] a full understanding of solvent effects on k_p would require that PLP−SEC experiments are carried out at similar radical chain lengths.

Conclusions

PLP−SEC investigations into the temperature and pressure dependence of the propagation kinetics for free-radical polymerizations of styrene in CO_2 provide no indication of any solvent effect. Comparison of k_p values determined for (meth)acrylate polymerization in solution of CO_2 and in bulk indicates that a solvent effect on k_p is restricted to systems where the polymer is not overly soluble in CO_2 *and* where significant *intra*segmental interactions occur.

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