Pressure and Temperature Dependence of Butyl Acrylate Propagation Rate Coefficients in Fluid CO_2

Sabine Beuermann,* Michael Buback, and Claudia Schmaltz

Institut für Physikalische Chemie, Universität Göttingen, Tammannstrasse 6, 37077 Göttingen, Federal Republic of Germany

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ABSTRACT: Propagation kinetics of butyl acrylate (BA) free-radical homopolymerization in fluid CO_2 has been studied by the PLP−SEC (pulsed laser polymerization−size-exclusion chromatography) method at pressures between 200 and 2000 bar and temperatures between −9 and 20 °C. The CO_2 content was close to 45 wt % in all experiments. As a consequence of the poor chain-transfer activity in solution of CO_2, the molecular-weight distributions of the polymer samples show well-resolved PLP structures with at least two, but in most cases three, distinct inflection points. At the p and T conditions of this work, the observed propagation rate coefficients (k_p) of BA in fluid carbon dioxide at CO_2 contents around 45 wt % are found to be about 40% below the corresponding bulk polymerization values. The activation volume and activation energy of k_p are, however, identical for bulk and solution (in CO_2) free-radical BA polymerizations within experimental accuracy. The origin of the solvent influence on the propagation reaction is discussed. The observed lower values of k_p in solution of CO_2 are assigned to the poor solvent quality of carbon dioxide, presumably resulting in a local monomer concentration at the site of the propagating radical which is smaller than the overall monomer concentration in the system.

Introduction

Supercritical carbon dioxide ($scCO_2$) has been demonstrated to be a promising alternate reaction medium for free-radical polymerization by DeSimone and coworkers.[1−3] These authors studied solution polymerizations of 1,1-dihydroperfluorooctyl acrylate and of siloxanes. With the exception of two studies,[4,5] literature however reflects only little interest in detailed kinetic investigations of free-radical polymerizations in $scCO_2$. In these two papers,[4,5] the PLP−SEC technique, a combination of pulsed laser polymerization (PLP) and of measurement of molecular-weight distribution (MWD) of the resulting polymer, by size-exclusion chromatography (SEC), has been used to deduce propagation rate coefficients, k_p, for polymerizations in fluid CO_2 of methyl methacrylate,[4,5] styrene,[4] and butyl acrylate.[5] The PLP−SEC procedure, which has been extensively used to determine k_p of free-radical polymerizations in bulk and in conventional solvents, is recommended as the method of choice by the IUPAC Working Party on "Modeling of Polymerisation Kinetics and Processes". Benchmark k_p data sets for styrene[6] and methyl methacrylate[7] bulk polymerizations have already been collated by this Working Party.

In PLP−SEC, the propagation rate coefficient k_p is derived via eq 1 from a characteristic degree of polymerization, L_i, which is directly available from the MWD.

$$L_i = ik_pc_Mt_0 \qquad i = 1, 2, 3, ... \tag{1}$$

where c_M is the monomer concentration and t_0 is the time between two successive laser pulses. As detailed elsewhere,[6] L_1 is best identified with the position of the inflection point on the low-molecular-weight side of the MWD peak maximum. To obtain reliable k_p values, the existence of a second L_2 or even a third L_3 inflection point at degrees of polymerization around $2L_1$ and $3L_1$ is required. The occurrence of such higher order inflection points serves as an internal consistency check of the PLP−SEC method.[6,8]

Our previous study[5] on butyl acrylate (BA) and methyl methacrylate (MMA) in fluid CO_2 showed that k_p clearly varies with CO_2 content and is by about 40% below the corresponding bulk value at initial monomer concentrations c_M below $c_M^0/2$, where c_M^0 is the bulk monomer concentration. For each monomer these experiments have been carried out only at a single set of p and T conditions, 200 bar and 10 °C for BA and 1000 bar and 30 °C for MMA. It was interesting to see whether the lowering of k_p in solution of CO_2 varies with polymerization pressure and temperature. To answer this question, within the present study PLP−SEC experiments on butyl acrylate in fluid CO_2 have been performed at pressures from 200 to 2000 bar and temperatures from −9 to 20 °C. The CO_2 content was kept (nearly) constant at around 45 wt % in all experiments. At such CO_2 contents, k_p of BA at 200 bar and 10 °C was measured to be 40% below the associated bulk value.[5] It should be noted that the authors in ref 4 observed no such clear change in k_p for styrene and MMA free-radical polymerizations in CO_2 at higher temperature (65 °C).

Studying BA instead of MMA is more challenging as acrylate PLP−SEC work provides difficulties in finding reaction conditions such that the resulting polymer MWD is controlled by the characteristic PLP pattern.[9−12] Laser pulsing needs to dominate chain-starting and chain-stopping events. This requirement is not easily achieved in acrylate bulk polymerization where k_p and also the rate of chain transfer to an acrylate monomer are high.[9,13] The problems may be partly overcome by PLP at a relatively low temperature or in solution of substances with low chain-transfer activity. CO_2 should be a particularly attractive solvent for PLP as chain-transfer reactions will not contribute to the chain-stopping events to any significant extent.[14] On the other hand, according to the evidence from the preceding study,[5] the propagation rate coefficient may vary with CO_2 content. The situation may thus be envisaged that

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PLP−SEC studies in fluid CO_2 allow for accurate k_p determinations with the obtained rate coefficients however being different from the bulk polymerization values.

The influence of (conventional) solvents on the propagation rate coefficient in MMA and in styrene polymerizations has recently been investigated by O'Driscoll et al.[15] and by Zammit et al.[16] The latter authors found variations in both Arrhenius parameters, the preexponential, A, and the activation energy, E_A, upon variation of solvent type and solvent content. Most of the solvents studied so far show either minor or mostly no changes in k_p. Carbon dioxide may be a notable exception to these findings. Studies into propagation rate coefficients for free-radical polymerizations of butyl acrylate in fluid CO_2 thus are of interest with respect to gaining more insight into solvent effects on k_p. It goes without saying that the results are also important for the modeling of free-radical polymerization reactions carried out in $scCO_2$.

Experimental Section

The monomer *n*-butyl acrylate (BA; >99%, stabilized with 0.0015 wt % hydroquinone monomethyl ether, Fluka Chemie AG, Buchs, Switzerland) was distilled over K_2CO_3 under reduced pressure to remove the inhibitor. The photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA; 99%, Aldrich-Chemie, Steinheim, F.R.G.) and carbon dioxide (CO_2; grade 4.5, Messer Griesheim, Krefeld, F.R.G.) were used without further purification.

The experimental setup for the preparation of the reaction mixture has already been described elsewhere.[5,17] The major components are a mixing autoclave, equipped with a magnetic stir bar and with a cooling device, and the optical high-pressure cell. CO_2 and BA containing the photoinitiator DMPA are mixed for at least 1 h. An HPLC pump keeps the pressure at a constant level of 300 bar while filling the optical high-pressure cell. After being filled, the high-pressure cell is disconnected from the pressure branch, inserted into the sample compartment of a Fourier Transform infrared (IR)/near-infrared (NIR) spectrometer (IFS 88, Bruker, Karlsruhe, F.R.G.) and subsequently into the laser irradiation assembly.

BA concentrations are determined via quantitative online NIR spectroscopy in the region of the C−H stretching first overtones.[5] The FT spectrometer was equipped with a tungsten lamp, a silicon-coated CaF_2 beam splitter, and a liquid nitrogen-cooled InSb detector. Data acquisition and processing are performed on a personal computer using the OPUS software provided by Bruker. A Blackman-Harris three-term function is applied for apodization. The initial concentrations of DMPA were between 2×10^{-3} and 4×10^{-3} mol·L^{-1}, and the initial butyl acrylate concentration was around 4 mol·L^{-1}. DMPA decomposition was induced by an excimer laser (LPX 210i, Lambda Physik, Göttingen, F.R.G.) at 351 nm (XeF line) with a laser pulse repetition rate, ν_R, of 100 Hz. The samples are subjected to laser pulsing for times sufficient to convert around 3% of the monomer into polymer. Monomer conversion is monitored by NIR spectroscopy after sequences of pulses are applied.

The final conversions (U) reached within the individual polymerizations are listed in Table 1 together with reaction temperature and pressure. At the low-conversion range examined in these experiments the monomer/polymer/CO_2 systems stays homogeneous. After irradiation, the reaction mixture is depressurized and the monomer/polymer mixture collected. To prevent further polymerization, hydroquinone is added. The polymer is then precipitated using methanol and is isolated.

Molecular-weight distributions have kindly been determined at the Laboratory of Polymer Chemistry at Eindhoven University of Technology by size-exclusion chromatography using two linear Shodex KF-80M columns. These analyses were performed at 40 °C with tetrahydrofuran as the eluent. Molecular-weight calibration is established via narrow polydispersity polystyrene (PS) standards (Polymer Labs, Mainz, F.R.G.). Via universal calibration[18] the MWDs "as PS" are transformed into MWDs of poly(butyl acrylate) using the Mark−Houwink (MH) constants a and K given in the literature:[9] $a = 0.716$ and $K = 11.4 \times 10^{-5}$ dL·g^{-1} for PS and $a = 0.700$ and $K = 12.2 \times 10^{-5}$ dL·g^{-1} for poly(butyl acrylate).

Table 1. Experimental Parameters and Results for Butyl Acrylate Polymerizations in Fluid CO_2

c_{BA} (mol·L^{-1})	T (°C)	p (bar)	U (%)	L_1 (10^2)	L_2 (10^2)	L_3 (10^2)	k_p (10^3(L·mol^{-1}·s^{-1}))
4.1	−1.1	200	2.8	2.04	4.31		5.1
4.0	−2.1	200	3.1	2.13	4.42	7.50	5.4
4.4	−1.5	1000	4.4	3.71	6.98	11.1	8.7
4.1	−1.6	1000	3.0	3.47	6.73	10.7	8.7
4.1	−0.5	2000	4.7	5.91	11.9	19.7	14.8
4.3	−1.6	2000	4.6	5.52	10.9	18.4	13.1
4.0	−8.0	1000	3.0	3.06	5.83	9.5	7.8
4.0	−8.9	1000	3.2	2.94	5.65	9.0	7.4
4.0	9.2	1000	3.4	4.86	9.39		12.5
4.1	9.7	1000	2.7	4.80	9.56	15.8	12.0
3.8	19.6	1000	2.9	5.77	11.8	16.9	15.3
4.0	19.7	1000	4.3	6.24	12.18		15.8

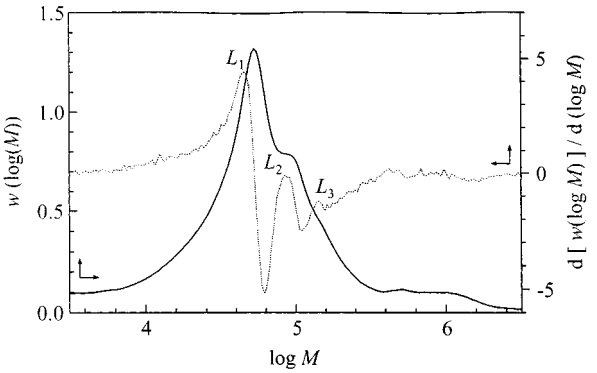

Figure 1. Polymer molecular-weight distribution (full line) and corresponding first derivative plot (dotted line) obtained for a butyl acrylate polymerization in CO_2 at −1 °C, 1000 bar, and an initial monomer concentration of 4.4 mol·L^{-1}.

Results and Discussion

The butyl acrylate PLP−SEC experiments have been carried out in the narrow range of initial monomer concentrations between 3.8 and 4.4 mol·L^{-1}. The molecular-weight distribution obtained for a polymerization at −1 °C, 1000 bar, and an initial BA concentration of 4.4 mol·L^{-1} is presented in Figure 1. A sharp peak with a pronounced second component at a higher molecular weight, close to log $M = 4.9$, and a weak shoulder at an even higher molecular weight, around log $M = 5.2$, are clearly seen. Also plotted in Figure 1, as a dotted line, is the first derivative of the MWD, to visualize (by the maxima on this curve) the position of points of inflection on the MWD which are required for the kinetic analysis via eq 1. The derivative plot exhibits three well-resolved such maxima, corresponding to the first three inflection points: L_1, L_2, and L_3. Table 1 lists for each experiment the PLP conditions: initial BA concentration, c_{BA}, polymerization temperature, T, polymerization pressure, p, monomer conversion, U, and the positions of the inflection points, L_1 and L_2, and in most cases also L_3. L_2 is by about a factor of 2 and L_3 by about a factor of 3 above L_1. The existence and the location of these higher order inflection points demonstrate that the consistency criteria for reliable

k_p determination are met by the PLP−SEC data of this work.

It should be noted that the MWDs of the present investigation are the first acrylate PLP−SEC data with a clear third inflection point, L_3. Lyons et al.[10] and Beuermann et al.[9] argued about the reasons for the poor PLP structure of acrylate SEC traces. The latter authors assigned the problems to the combined action of a high k_p and of a high rate coefficient for chain transfer to monomer, $k_{tr,M}$. With increasing temperature, the characteristic degree of polymerization determined by chain transfer to monomer, DP_{tr}, and the degree of polymerization determined by PLP, L_1, are approaching each other.[9] Under such conditions it becomes rather difficult, or may even be impossible, to detect the position of the higher order inflection points, L_2 and L_3. Further, the PLP structure of the MWDs may also be obscured because of "unsuitable" termination rates. This however does not seem to be the case with the acrylates because the presence of a well-resolved PLP structure in the MWD was found to be independent of the free-radical concentration: BA studies by Beuermann et al.[9] at temperatures up to 30 °C showed MWDs with a well-resolved PLP structure at widely varying free-radical concentrations. It is observed within the present study that the PLP structure is also insensitive toward changing pressure. As a variation in pressure by almost 2000 bar considerably changes the termination rate coefficient,[17,19,20] this finding supports the view that the characteristic features in the MWD of acrylate PLP−SEC samples are not controlled by the termination rate.

As was shown in the PLP−SEC studies on MMA, vinyl acetate and BA free-radical polymerizations,[9] the ratio DP_{tr}/L_1 should be well-above unity in order to have a pronounced PLP structure in the MWD. DP_{tr}/L_1 may be expressed by

$$\frac{DP_{tr}}{L_1} = \frac{1}{t_0(k_{tr,M}c_M + k_{tr,CTA}c_{CTA})} \qquad (2)$$

where c_{CTA} and $k_{tr,CTA}$ refer to the concentration and to the transfer rate coefficient of a chain-transfer agent (CTA), respectively.

Equation 2 adequately describes the observations made in PLP−SEC experiments on MMA.[9] Upon the addition of an effective chain-transfer agent, the PLP structure is obscured. Increasing the CTA concentration, according to eq 2, lowers DP_{tr}/L_1 and leads to the gradual disappearance of the third and subsequently of the second point of inflection. Addition of CO_2, as within the present work, has the opposite effect on transfer rates: CO_2 as a medium of very low transfer activity ($k_{tr,CTA}$ close to zero), replaces BA which shows considerable chain transfer to monomer activity[21] that may be further enhanced by impurities contained in the BA monomer.[13] In going from BA bulk polymerization to solution polymerization in fluid CO_2, the sum of the two terms in the denominator of eq 2 decreases and DP_{tr}/L_1 is enhanced. As a consequence, the PLP structure of the MWD becomes more pronounced and a distinct second and also third inflection point are seen. The reduction in k_p by 40% with respect to bulk free-radical polymerizations additionally favors the quality of PLP−SEC studies in fluid CO_2 as the molecular-weight (MW) range that is dominated by PLP is shifted to smaller MWs. The MWD regions controlled by PLP and chain-transfer activity are hence more separated.

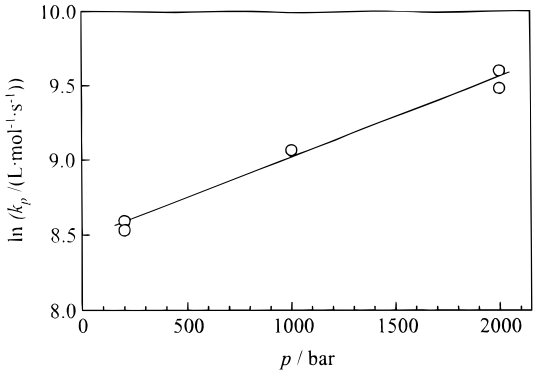

Figure 2. Pressure dependence of k_p for BA polymerizations in carbon dioxide at −1 °C and 45 wt % CO_2. The fitted line (eq 2) is obtained by linear regression.

In summary, performing PLP−SEC experiments in solution of CO_2 is advantageous with respect to bulk experiments as the ratio DP_{tr}/L_1 is enhanced: Transfer reactions become less important, which increases DP_{tr}, and k_p is reduced which lowers L_1.

The k_p data that have been obtained within the present investigation are given in the last column of Table 1. These numbers are determined via eq 1 by considering the L_1 positions only. The k_p data are assumed to be accurate within ±20% with contributions to this error resulting from uncertainties in knowing the Mark−Houwink coefficients (±10%) and in determining c_{BA}, the BA concentration (±10%). The latter quantity is given by the arithmetic mean of BA concentrations measured (spectroscopically) before and after applying the laser pulsing required to reach the final monomer conversion given for each experiment in the fourth column of Table 1.

Pressure Dependence of k_p. Propagation rate coefficients, k_p, of butyl acrylate in solution of CO_2 have been determined for pressures between 200 and 2000 bar at −1 °C. In Figure 2, ln k_p is plotted versus pressure. The experimental points fit to a straight line represented by eq 3:

$$\ln(k_p/(\mathrm{L{\cdot}mol^{-1}{\cdot}s^{-1}})) = 8.47 + 5.41 \times 10^{-4}(p/\mathrm{bar}) \qquad (3)$$

$$(45\ \mathrm{wt\ \%\ CO_2};\ -1\ ^\circ\mathrm{C};\ 200 \le p \le 2000\ \mathrm{bar})$$

From the slope of the straight line, an activation volume, $\Delta V^{\ddagger} = -RT(\mathrm{d}(\ln k)/\mathrm{d}p)_T$, of $\Delta V^{\ddagger}(k_p) = (-12.2 \pm 1.5)$ $\mathrm{cm^3{\cdot}mol^{-1}}$ is obtained. The corresponding activation volume for BA bulk polymerization has not been determined. Previous work into k_p of alkyl acrylates[12] (and also of alkyl methacrylates[22,23]) however showed that the activation volumes are virtually identical within each of the two monomer families. Thus, $\Delta V^{\ddagger}(k_p)$ of the BA bulk polymerization should be close to the $\Delta V^{\ddagger}$ values reported for the bulk polymerizations of methyl acrylate and dodecyl acrylate, (-11.2 ± 0.7) $\mathrm{cm^3{\cdot}mol^{-1}}$ and (-11.7 ± 1.8) $\mathrm{cm^3{\cdot}mol^{-1}}$, respectively.[12] Taking the limits of experimental accuracy into account, both these numbers agree with $\Delta V^{\ddagger}(k_p)$ measured in solution of CO_2. No difference is thus seen between $\Delta V^{\ddagger}(k_p)$ of BA in bulk and in solution of CO_2.

Temperature Dependence of k_p. The temperature dependence of k_p for BA polymerizations in CO_2 has been examined between −9 and 20 °C at 1000 bar. The resulting data are given as an Arrhenius plot in Figure

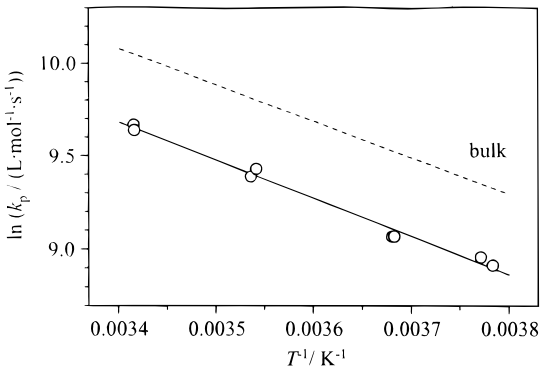

Figure 3. Temperature dependence of k_p for BA polymerizations in carbon dioxide (45 wt %) at 1000 bar (circles). The dashed line represents the corresponding bulk values of k_p obtained from refs 9 and 10. The full line (eq 3) is obtained by linear regression.

3. The data points are well-fit by the following linear expression:

$$\ln(k_p/(\mathrm{L \cdot mol^{-1} \cdot s^{-1}})) = 16.63 - 2044(T/\mathrm{K})^{-1} \quad (4)$$

(45 wt % CO_2, 1000 bar; $-9 \le T \le 20$ °C)

Equation 4 is associated with an activation energy of $E_A(k_p) = (17.0 \pm 1.2)$ kJ·mol^{-1}. This value, which has been obtained for polymerization at 1000 bar, may be converted into the corresponding ambient pressure value, E_A (k_p, 1 bar), via eq 5:

$$E_A(k_p, 1\ \mathrm{bar}) = E_A(k_p, 1000\ \mathrm{bar}) - (p - 1\ \mathrm{bar})\Delta V^{\ddagger}(k_p) \quad (5)$$

With $\Delta V^{\ddagger}(k_p) = -12.2$ cm^3·mol^{-1} (see eq 3), the activation energy at ambient pressure is obtained to be: $E_A(k_p, 1\ \mathrm{bar}) = (18.2 \pm 1.5)$ kJ·mol^{-1}. This number may be compared with the activation energy derived from literature data for bulk polymerizations of BA at ambient pressure reported by Lyons et al.[10] and Beuermann et al.[9] The combined data set (85 individual data points) from both groups yields an activation energy of $E_A(k_p, 1\ \mathrm{bar}) = (17.4 \pm 0.25)$ kJ·mol^{-1}. Thus, as with the activation volume, also for the activation energy no significant difference is seen between BA polymerization in bulk and in solution of CO_2.

In absolute value, however, k_p is clearly different for the two reaction media, bulk and mixture with CO_2, as is illustrated in Figure 3. The dashed line represents the fit to the combined BA bulk polymerization data set (Lyons et al.[10] and Beuermann et al.[9]) which has been converted to 1000 bar, the pressure applied in the CO_2 solution experiments, via the activation volume of the bulk polymerization. The bulk k_p data are by about 40% above the propagation rate coefficients measured in mixtures with 45 wt % CO_2, which fully agrees with the observation from our previous study.[5] The data in Figure 3 suggest that the difference between bulk and solution k_p is primarily in the preexponential factor, whereas the activation energies agree within experimental accuracy. It should, however, be noted that the number and the precision of k_p data measured in CO_2 solution is not sufficient to safely assign, (e.g., by the statistically relevant procedure of calculating 95% confidence ellipsoids from the experimental rate coefficients in the manner suggested by van Herk)[24] the difference to either the preexponential or to $E_A(k_p)$.

The experimental observations may be summarized: BA propagation rate coefficients for polymerizations in bulk and in fluid carbon dioxide, at CO_2 contents above 45 wt %, are dissimilar. The difference appears to be primarily due to the preexponential factor $A(k_p)$, whereas both the activation energy, $E_A(k_p)$, and activation volume, $\Delta V^{\ddagger}(k_p)$, are identical within the limits of experimental accuracy.

The experiments in CO_2 solution provide another example for a solvent dependence of k_p. The invariance of the propagation rate coefficient toward the type (and the concentration) of a solvent, which appeared to be a well-established finding backed by an extended set of k_p studies, in particular on MMA dissolved in methanol,[25] ethanol,[26] ethyl acetate,[25] toluene,[27] and 2-butanone[27] is thus not generally valid. Especially noteworthy with our BA k_p studies in solution of CO_2 is the observation of a clear decrease in k_p with respect to the bulk polymerization value. Only a single example for a decrease of k_p in solution has been reported so far: Using chlorobenzene as a solvent, k_p has been found to be below the bulk value by 7% (which is within the limits of experimental accuracy). With this exception, the changes in k_p for polymerization in solution reported in the paper by Zammit et al.[16] are enhancements which may be as large as 75% for MMA and styrene homopolymerizations in benzyl alcohol and in *N*-methyl pyrrolidinone.

Before the solvent dependence of k_p observed with CO_2 is discussed, it should be pointed out that these effects, although being clear and significant, are by no means spectacular. It is the high accuracy in the k_p measurement provided by the PLP−SEC technique that allows these detailed effects to be safely detected.

Arguments for a solvent dependence of the propagation rate coefficients have been presented by Kamachi.[28] They encompass influences originating from (1) copolymerization with the solvent, (2) polarity, (3) transfer reactions, (4) interaction between the polymer and solvent, (5) interaction between the monomer and solvent, and (6) complexation between the propagating free radical and the solvent. As has been outlined in the preceding paper,[5] the observed variation of k_p with CO_2 content cannot be explained by arguments (1)−(3). That the changes in k_p result from interactions of the solvent with the polymer, with the monomer, or with the propagating free radical according to arguments (4)−(6), respectively, is also not overly likely as no significant interactions between CO_2 and these species are expected to occur. The insensitivity of $E_A(k_p)$ and of $\Delta V^{\ddagger}(k_p)$ toward the reaction medium, polymerization in bulk or in solution of CO_2 supports the view that the dynamics of the propagation step is essentially the same in both media.

The reduction of k_p upon adding CO_2 to pure BA (and to pure MMA[5]) may result from an associated decrease in solvent quality of the polymerization medium. In extending arguments of Dionisio et al.[29] on the influence of polymer coil size and segment density on free-radical termination rates, one may assume that solvent quality and thus coil size also influence k_p. Under conditions of poor solvation, the free-radical chain-end may be shielded within the tightly coiled macroradical, and thus the local monomer concentration, $c_{M,loc}$, inside the domain of the propagating radical is smaller than the

overall monomer concentration in the system. This view is in agreement with discussions on preferential solvation for example by Kuchanov and Russo[30] and Kratochvil et al.[31] The latter authors report that local monomer concentrations in the vicinity of the propagating radical are dependent on the solvent quality. Similar arguments are used to explain solvent influences on copolymer composition (e.g., by Harwood[32] and Semchikov[33]).

Equation 1 shows that it is the product $k_p c_M$ which is determined from the experimental quantities L_1 and ν_R by PLP−SEC. The experimentally observed k_p value will be smaller than the true k_p value, if $c_{M,loc}$ is below the overall monomer concentration c_M. Therefore, the observed reduction of k_p in the presence of CO_2 may reflect a variation in $c_{M,loc}$. However, presently a measure for $c_{M,loc}$ is not available. As local monomer concentrations cannot be quantified, in the remainder of the text we will continue to use the wording "solvent effect on k_p". The reader should keep in mind that this dependence may result from a variation of $c_{M,loc}$ in the presence of a solvent.

No major changes in k_p are expected to emerge from such a thermodynamic-type contribution. This is in agreement with the observation of only small effects on k_p even upon a significantly varying molecular environment of the free radical (e.g., by replacing BA molecules by CO_2). In the majority of solution studies no clear variation of k_p will occur as the solvents for a particular polymer will not be too dissimilar in solvent quality and will not be too different from the solvent quality of the monomer in cases where the monomer is a suitable solvent medium for the associated polymer.

Such a thermodynamic argument would explain why only rather few examples of a solvent dependence of k_p are found and why the effects are relatively small. A clear difference between bulk and solvent k_p may be expected in cases where the solvent qualities are quite dissimilar or where the steric requirements of a solvent largely deviate from the situation with the monomer (e.g., cyclic vs linear structures). It goes without saying that the solvent quality (and thus coil size and segmental density) argument does not have to be the single reason why k_p may vary with the solvent environment. In solvents of strong and specific interactions with either the polymer, the monomer, or the free-radical chain-end other effects may also be operative. It should be noted that the thermodynamic argument with CO_2 as the solvent concerns a special situation in that the interactions with CO_2 are rather weak as compared to the reference situation of polymer−monomer interactions (during bulk polymerization).

The difference in observed k_p being primarily in preexponential factor and not in activation energy, as shown in Figure 3 for the bulk and solution (in CO_2) polymerization of BA, resembles the situation met within the acrylate and methacrylate families where, toward a larger ester size, the Arrhenius lines are shifted to higher k_p with this change also being assigned primarily to an increase in the preexponential.[22,34,35] There is considerable temptation to assign this variation to the same solvent quality argument as has been used to explain the influence of CO_2 on observed k_p. It is known that dodecyl acrylate homopolymerizations may be carried out in homogeneous phase to much higher degrees of monomer conversion than methyl acrylate homopolymerizations. This indicates that solvent quality is enhanced toward a larger size of the ester group. The increase in k_p that is found in going from methyl to dodecyl acrylate[12] thus, at least in part, may also be due to an increase in polymer coil size and an associated lowering of segmental density of the macroradical. A quantitative comparison of the effects on k_p (a) within the acrylate family and (b) for BA with and without CO_2 being present cannot be made, as the changes in bulk k_p within the acrylate family may originate from size effects of the free radical or of the monomer, which are both varied in going, for example, from methyl acrylate to dodecyl acrylate.

To further test the validity of the explanation of solvent-induced changes of k_p resulting from solvent quality and coil size, the measurements of k_p in CO_2 solution should be extended over a larger temperature range, in which solvent quality may significantly change. Such experiments for styrene polymerizations are underway in our laboratory.

As the suggested changes in coil size should be strongly reflected in the termination rate coefficient, also the k_t of free-radical polymerizations in fluid CO_2 should be studied. A series of k_t data which has already been measured for BA in our group[17] is indeed strongly indicative of such a decrease of coil size in CO_2 solution. Obviously online scattering experiments during polymerization would be particularly helpful toward resolving matters concerning coil dimensions.

Conclusions

The PLP−SEC technique has been used to measure the propagation rate coefficient of BA in solution of carbon dioxide (45 wt % CO_2) as a function of pressure and temperature. The observed k_p values (at identical p and T) are by about 40% below the corresponding bulk polymerization data. The activation volume and the activation energy of k_p are almost identical to the corresponding bulk polymerization values. As the PLP−SEC experiment measures the product of $k_p c_M$, the observed change cannot be safely assigned to either k_p or c_M. There is, however, some evidence that the local monomer concentration at the radical site differs from bulk c_M whereas k_p is not significantly different in both CO_2 solution and in bulk.

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