Propagation Kinetics in Free-Radical Polymerizations

Sabine Beuermann

Institute of Physical Chemistry, Georg-August University Göttingen
Tammannstrasse 6, 37077 Göttingen, Germany

Summary: The combination of pulsed laser initiated polymerizations (PLP) with analysis of the generated polymer by size-exclusion chromatography (SEC) yields reliable individual rate coefficients for polymerizations of a large number of monomers in bulk and in solution. PLP-SEC experiments carried out in the presence of $scCO_2$ as a solvent show no unambiguous trend: while a significant reduction of k_p is seen for some monomers, e.g. acrylates, k_p for monomers such as vinyl acetate and styrene is not affected. It is suggested that the influence of CO_2 on acrylate k_p is not a true kinetic effect and that the experimental findings may be understood in terms of the occurrence of local monomer concentrations in the vicinity of the propagating radical. It is discussed that such local monomer concentrations may also contribute to a better understanding of why k_p increases with ester size within the acrylate or within the methacrylate family, and why k_p frequently is influenced by the initiating laser pulse repetition rate.

Introduction

With the advent of pulsed-laser initiated polymerizations (PLP) reliable rate coefficients for free-radical polymerizations have become available. Especially the combination of PLP with polymer analysis by size-exclusion chromatography (SEC), as introduced by Olaj and coworkers,[1,2] provided propagation rate coefficients, k_p, for a large number of monomers. Using the PLP-SEC technique, an evenly spaced sequence of laser pulses is applied to a monomer/photoinitiator system and a small initial monomer conversion, typically of two or three per cent, is reached. The almost instantaneous production of free radicals by each laser pulse causes an enhanced termination probability for radicals from the preceding pulse(s). This situation gives rise to a characteristic structure of the molecular weight distribution (MWD), as is illustrated in Figure 1, where the weight fraction w is plotted vs. the logarithm of molecular weight (full line), $\log_{10} M$. The polymer originates from a dodecyl acrylate (DA) polymerization in solution of 36 wt.% fluid CO_2 at – 4 °C, 200 bar, using a laser pulse repetition rate of 100 Hz.[3] k_p is derived via Eq. (1) from a characteristic degree of polymerization, L_i, which is directly obtained from the molecular weight distribution (MWD).

 CCC 1022-1360/00/$ 17.50+.50/0

$$L_i = i \cdot k_p \cdot c_M \cdot t_0 \qquad i = 1, 2, 3, \ldots \qquad (1)$$

where c_M is the monomer concentration and t_0 is the time between two successive laser pulses. As detailed elsewhere,[4] in most cases L_1 is best identified with the position of the inflection point on the low molecular weight side of the MWD peak maximum. The inflection point of the MWD at L_1 is characterized by the first maximum of the derivative plot, given as a dotted line in Figure 1. In order to obtain reliable k_p values, the existence of a second or even a third inflection point at degrees of polymerization around $L_2 = 2 \cdot L_1$ and $L_3 = 3 \cdot L_1$ is required. The occurrence of such higher order inflection points serves as a consistency check of the PLP-SEC method.[4]

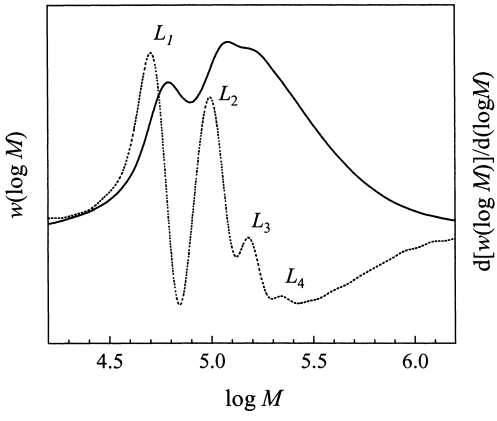

Figure 1:
Molecular weight distribution (full line) and corresponding derivative plot (dotted line) for a poly (dodecyl acrylate) sample generated at – 4°C, 200 bar, and a laser pulse repetition rate of 100 Hz in the presence of 36 wt.% fluid CO_2.

In this contribution a short overview on the propagation rate coefficients available for bulk homopolymerizations will be given, followed by a discussion of the influence of fluid or supercritical (sc) CO_2 on propagation kinetics. Besides being an attractive new solvent for technical applications, CO_2 has been chosen as a solvent for mechanistic studies, because the physico-chemical properties of fluid CO_2 may be tuned over a wide range. It is expected that CO_2 will form complexes with neither the monomer nor with the macroradical or with the polymer. Because it is known from phase behavior measurements that polystyrene and poly(meth)acrylates show only limited solubility in $scCO_2$,[5] the use of CO_2 as solvent medium should also allow for investigations into the influence of solvent quality and thus the influence of chain geometry on the propagation reaction. (Note: Although CO_2 is a poor solvent for the polymers under investigation, PLP-SEC experiments are carried out in homogenous phase due to the typically low

degrees of monomer conversion.)

Further, it will be discussed whether the findings for CO_2 as a solvent have an implication for polymerizations in conventional solvents or in bulk.

Polymerizations in Bulk

Since 1987, when the PLP-SEC technique was introduced first,[1] the bulk homopolymerization of a large number of monomers has been studied. After focussing on k_p for styrene and methyl methacrylate polymerizations in the early studies,[4,6] the investigations were extended to methacrylate monomers with longer alkyl,[7] cyclic[8,9] or functional ester groups.[8,9] In addition, substituted styrenes,[10] various acrylates,[11,12,13,14] vinyl esters,[15,16] and recently, itaconates[17,18] have been studied.

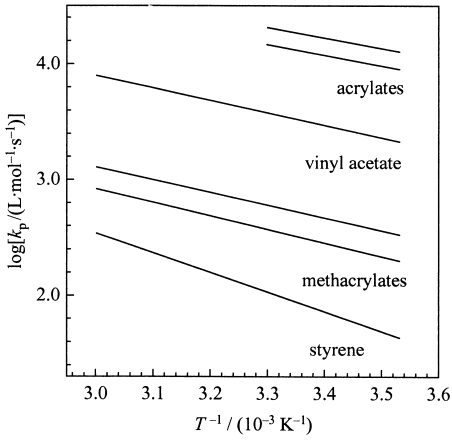

Figure 2:
Arrhenius diagram of k_p for styrene, vinyl acetate, alkyl acrylates, and alkyl methacrylate at ambient pressure. For details and references see text.

Figure 2 shows the variation of k_p with temperature for various monomer types. The upper lines given for acrylates and methacrylates refer to the dodecyl ester, whereas the lower lines represent the methyl esters. In case of the acrylates k_p data have been determined successfully only for temperatures of at most 30°C. Figure 2 indicates that variations in k_p due to the size of the ester group within the family of the methacrylates or within the family of the acrylate monomers are only small compared to variations in k_p for different monomer classes. The activation energies of k_p are about 22 kJ·mol^{-1} for alkyl methacrylates[7] and about 15 kJ·mol^{-1} for the acrylates.[11,12,13,14] Within the family of the acrylates and within the family of the methacrylates the activation energies, E_A, are invariant with the size of the ester group. This finding is not surprising, because of the distance to the reactive center it is unlikely that the size of the

ester group will have a significant impact on the stability of the radical or the reactivity of the monomer.

Investigations into the pressure dependence of k_p revealed a very similar variation of k_p with pressure, p, for acrylates, vinyl acetate, and styrene, whereas a stronger dependence was seen for the methacrylates, which is reflected by activation volumes of $\Delta V^{\#}(k_p)$ of -16 $cm^3 \cdot mol^{-1}$ for the methacrylates compared to -12 $cm^3 \cdot mol^{-1}$ for the other monomers. This behavior is supposed to originate from differences in steric hindrance in the transition state due to the additional methyl substituent at the double bond in the methacrylate monomers.[19]

Polymerizations in Solution of Fluid or Supercritical CO_2

In addition to bulk polymerizations, reactions in solution have been investigated, too. While early studies indicated that k_p is not influenced by the solventm,[2,20] more recent studies showed that for particular monomer-solvent systems a strong solvent effect may be seen.[21] Our investigations into polymerizations in solution of CO_2 revealed that for butyl acrylate (BA) and methyl methacrylate (MMA) a significant decrease in k_p occurs.[22,23]

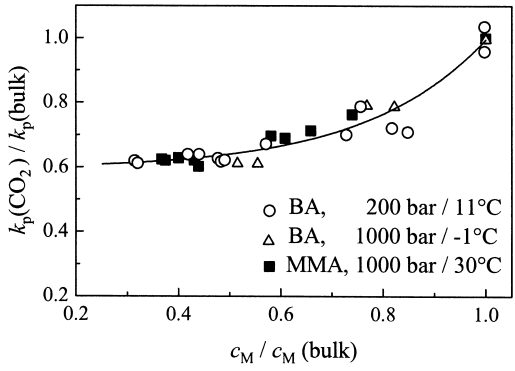

Figure 3: Variation of the propagation rate coefficient k_p with monomer concentration for MMA (open marker) and BA (filled marker) polymerizations in CO_2. k_p values and monomer concentrations are given relative to the corresponding bulk values.[22]

As an example, Figure 3 depicts the influence of CO_2 on k_p for MMA and BA homopolymerizations. The diagram shows the dependence of the ratio of k_p for experiments in solution of CO_2, $k_p(CO_2)$, over k_p in bulk reactions at identical p and T on the monomer concentration, represented by the ratio of c_M in the presence of CO_2, $c_M(CO_2)$, over c_M in bulk. For both monomers and the indicated conditions of p and T, a

distinct reduction of 40 % in $k_p(CO_2)/k_p$(bulk) upon addition of CO_2 is observed. For $c_M(CO_2)/c_M$(bulk) ranging from 0.3 to 0.6 a constant value of 0.6 is observed for $k_p(CO_2)/k_p$(bulk).

Additional investigations into methyl acrylate (MA) and dodecyl acrylate (DA) homopolymerizations also showed a reduction of k_p in the presence of CO_2.[3] Table 1 indicates the maximum variation of k_p in the presence of CO_2. It is clearly seen that the reduction in k_p is less pronounced for DA, the monomer with the longest ester group. Studies of the p and T dependence of k_p at CO_2-contents around 40 wt.% resulted in values for E_A, and $\Delta V^{\#}$, which are the same as observed in bulk polymerizations within experimental accuracy. In contrast to the findings for the acrylates, k_p in homopolymerizations of styrene[24] and vinyl acetate[25] (VAc) is not affected by the presence of CO_2.

Table 1: Activation energies, E_A, activation volumes, $\Delta V^{\#}$, and the ratio of k_p for reactions in solution of CO_2 to k_p for bulk experiments. E_A and $\Delta V^{\#}$ refer to polymerizations in bulk and in solution of CO_2. [a] $T < 30°C$, for details see refs. [3,22]; [b] 1000 bar; [c] 40 wt.% CO_2; [d] 23°C, 200-1900 bar; [e] compare Fig. 3; [f] 35 wt.% CO_2, 23°C, 200-1500 bar; [g] 80°C; [h] 300 bar; [i] 80°C, 300 bar; [j] 25°C; [k] ambient pressure; [l] 25°C, 1000 bar.

monomer	MA[3]	BA[22]	DA[3]	styrene[24]	VAc[25]
$\Delta V^{\#}$/cm^3·mol^{-1}	-12 ± 1.5 [a]			-11 ± 1.8 [g]	-10 ± 0.9 [j]
E_A / kJ·mol^{-1}	15 ± 2.0 [b]			31 ± 3.2 [h]	20.5 [k] [16]
$k_p(CO_2/k_p$(bulk)[c]	0.55 ± 0.1 [d]	0.60 ± 0.1 [e]	0.75 ± 0.1 [f]	1.0 ± 0.1 [i]	1.0 ± 0.2 [l]

In order to understand these findings it should be considered that k_p values are derived from Eq. (1), with the experimentally accessible quantities L_1, generally derived from SEC measurements, and t given by the laser pulse repetition rate. Thus, actually the product of k_p and c_M is measured in PLP-SEC experiments: $k_p \cdot c_M = L_1 / t_0$. As a consequence, variations of k_p are implied, if c_M at the site of the propagation reaction is not identical with the overall or analytical monomer concentration c_M in the system. Based on the fact that E_A and $\Delta V^{\#}$ are not significantly changed in the presence of CO_2, it may thus be assumed that the observed reduction in k_p is not entirely a true kinetic effect. Instead, local monomer concentrations, $c_{M,loc}$, are suggested to occur in the vicinity of the propagating radical chain-end,[22,23] caused by the presence of CO_2. Therefore, an apparent solution k_p results from analysis of the PLP-SEC data due to identifying c_M in Eq. (1) with the overall monomer concentration c_M in the system.

In order to clarify the following discussion the analytical or overall monomer concentration is defined as $c_{M,a}$, the experimentally derived apparent propagation rate coefficient as $k_{p,exp}$, and the true kinetic propagation rate coefficient as $k_{p,kin}$. The relations between monomer concentrations and propagation rate coefficients are as follows:

$$L_1 / t_0 = k_{p,kin} \cdot c_{M,loc} = k_{p,exp} \cdot c_{M,a}. \quad (2)$$

The occurrence of local monomer concentrations may be understood considering a competition of (a) *intra*molecular interactions of polymer segments with other polymer segments of the same macroradical and (b) *inter*molecular interactions between polymer segments with monomer or CO_2 molecules. If *intra*segmental interactions within the polymeric radical are favored, the effective local monomer concentration in the vicinity of the propagating chain end is smaller than the overall monomer concentration in the system. In styrene polymerizations, where strong polar interactions between polymer segments are absent, a reduction in effective local monomer concentration compared to the overall monomer concentration should not occur. Thus, the overall monomer concentration $c_{M,a}$ should adequately represent c_M in Eq. (1). In acrylate systems interactions of polar segments are expected to be particularly pronounced for MA, whereas in DA systems the extent of *intra*segmental interactions should be decreased due to shielding effects of the large ester chain. This is reflected by a 45 % reduction of $k_{p,exp}$ observed for MA and by a 25 % reduction of $k_{p,exp}$ seen in DA polymerizations in the presence of CO_2.

According to these arguments, CO_2 should also lead to a decrease in $k_{p,exp}$ of VAc polymerizations, because *intra*segmental interactions between polymer segments should be operative in VAc polymerizations. However, $k_{p,exp}$ values for VAc polymerizations in bulk and in solution of CO_2 are the same.[25] The reason behind this observation probably is that CO_2 favorably interacts with poly(vinyl acetate) (PVAc)-segments. From phase behavior measurements of PVAc-CO_2 systems it is known that $scCO_2$ is a good solvent for the polymer.[26] Thus, it may be concluded that CO_2 solvates the polymeric radical in a similar way as the monomer, which is as well a good solvent for the polymer. As a consequence, for VAc polymerizations in $scCO_2$ local monomer concentrations are not expected to be different from bulk experiments. In contrast to PVAc, the isomeric poly(methyl acrylate) (PMA) has a much lower solubility in $scCO_2$.[26] Thus it may be concluded that interactions between PMA polymer segments

with CO_2 are less favorable. $c_{M,loc}$ is smaller than the overall monomer concentration in MA polymerizations. Investigations into the propagation rate coefficients of *n*-alkyl methacrylates also indicate a reduction of $k_{p,exp}$ for MMA, BMA, and DMA polymerizations in solution of CO_2.[27]

The findings for polymerizations in solution of CO_2 may be summarized as follows: An apparent solution propagation rate coefficient $k_{p,exp}$ will be derived from PLP-SEC data by identifying c_M in Eq. (1) with overall monomer concentrations $c_{M,a}$ in cases where polar *intra*segmental interactions are operative, and where at the same time, the interactions between CO_2 molecules and polymer segments are clearly different from the ones between monomer molecules and polymer segments. The discussion of local monomer concentrations is based on the assumption that the intrinsic kinetic propagation rate coefficient $k_{p,kin}$ in solution of CO_2 and in bulk are not significantly different, which seems to be fulfilled because activation energy and activation volume are identical for polymerizations in bulk and in solution of CO_2 in the studied p and T range. In the future experiments should be extended to higher p and T, since it is expected that the solvation of the growing radical by its environment will change, especially at higher temperatures.

The discussion of local monomer concentrations is in agreement with publications on preferential solvation[28] and on the solvent influence on copolymer composition.[29]

In the remainder of this text it will be discussed, whether the occurrence of local monomer concentrations may explain other findings from PLP-SEC experiments, e. g. why does $k_{p,exp}$ frequently increase with the initiating laser pulse repetition rate, ν, or why does $k_{p,exp}$ increase with the size of alkyl ester groups within the family of the acrylates or within the family of the methacrylates?

1. Increase of k_p with the initiating laser pulse repetition rate

The discussion of local monomer concentrations originating from differences in polymer solvation leads to the expectation that other factors affecting the solvation of the polymer molecule should also influence the propagation kinetics. Such a factor is the initiating laser pulse repetition rate as a means of controlling polymer molecular weight. Early PLP experiments, however, did not show a systematic variation of $k_{p,exp}$ with ν since mostly very similar ν have been used, often due to experimental limitations. The invariance of $k_{p,exp}$ with ν was in accordance with the expectation that $k_{p,exp}$ should not be influenced by the laser pulse repetition rate. Initially, $k_{p,exp}$ being constant with the

laser pulse repetition rate has been put forward as a consistency criterion[a] for finding suitable PLP conditions.[4,6] Extending PLP-SEC experiments to a larger number of monomer systems and to more extensively varied reaction conditions revealed that $k_{p,exp}$ may increase with ν, if ν is varied over a wide range. Actually, it seems to be the common behavior to observe a slight increase of $k_{p,exp}$. Invariance of $k_{p,exp}$ with ν seems to be the exception, e.g. $k_{p,exp}$ for 2-hydroxypropyl methacrylate polymerizations.[30] More recent PLP studies employing largely differing ν show an even stronger impact of ν on $k_{p,exp}$. For example, PLP-SEC experiments in solution of $scCO_2$ showed an increase of 25 % in going from 25 to 60 Hz for styrene - BA copolymerizations.[31] The results are shown in Figure 4: On the left hand side $k_{p,exp}$ is given as a function of ν and on the right hand side the associated variation of $k_{p,exp}$ with the molecular weight at the position of the first point of inflection, M_1, is shown. The results presented in Figure 4 demonstrate the strong influence of ν and thus molecular weight on $k_{p,exp}$.

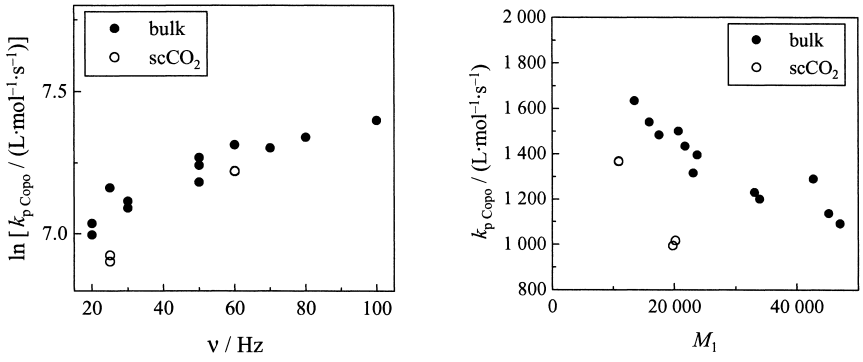

Figure 4: Propagation rate coefficients $k_{p,copo}$ for styrene-BA copolymerizations in bulk and in solution of 41 wt.% CO_2 at 80°C, 300 bar and a styrene content of $f_s = 0.5$ in the monomer feed as a function of the initiating laser pulse repetition rate ν and the molecular weight M_1 at the position of the first point of inflection.[31]

In addition, for MMA polymerizations it was observed that the effect of ν is more pronounced for polymerizations in the presence of CO_2.[27] Especially the observation of a superposition of a solvent and laser pulse repetition rate effect on $k_{p,exp}$ suggests that both effects should have the same origin. While there is no doubt that addition of a

[a] In the light of the observed variation of k_p with the initiating laser pulse repetition rate, other consistency criteria should be preferred, e.g. the ratio of L_1/L_2 should be around 0.5 indicating that the shape of the molecular weight distribution is controlled by the periodically changing radical concentration and thus periodically altered termination probability.

solvent to a polymerizing system will change the solvation of the growing polymeric radical, it is less obvious that variations in ν may also impact the solvation of the growing radical: The choice of ν directly controls the polymer molecular weight and thus, since polymer molecular weight and the geometry of the macromolecules are strongly correlated, the solvation of the polymer molecules will as well be changed.

Interestingly, in MMA homopolymerizations yielding low molecular weight polymers no difference in $k_{p,exp}$ data for polymerizations in bulk and in solution of $scCO_2$ is seen.[27,32] In contrast, polymerizations resulting in higher polymer molecular weights show a clear decrease of $k_{p,exp}$ in the presence of CO_2 compared to results from bulk experiments.[22,27] This behavior may be due to the better solubility of the polymers with lower molecular weight in CO_2. Thus, the polymer is better solvated by CO_2 and *intra*molecular interactions are expected to occur to a lesser extent as for the high molecular weight material. This explanation is in line with the vinyl acetate results, where the invariance of $k_{p,exp}$ in the presence of CO_2 is explained by the good solubility of the polymer and thus good solvating power of CO_2 for the polymer molecules.

Recently, Olaj et al. studied the influence of ν on $k_{p,exp}$ for MMA bulk polymerizations and styrene polymerizations in bulk and in solution of toluene, cyclohexane, and ethyl acetate.[33] In these experiments also a significant variation of k_p with M_1 is seen: $k_{p,exp}$ values increase with decreasing M_1 by up to 30 to 40%. The results are explained in terms of excluded volume effects of polymer segments and an associated occurrence of $c_{M,loc}$ in the vicinity of the propagating radical chain end.

2. Increase of k_p with the size of alkyl ester group

As discussed for solution polymerizations in CO_2, in bulk polymerizations of MA and MMA strong *intra*molecular interactions between polymer segments may occur. This behavior is not only restricted to reactions in CO_2, but also applies to polymerizations in conventional solvents or in bulk. The interactions are expected to result in an effective displacement of a large fraction of monomer molecules from the surroundings of the free-radical chain and thus the occurrence of a local monomer concentration, which is below the total monomer concentration in the system. In polymerizations of dodecyl acrylate and dodecyl methacrylate (DMA) the long non-polar ester groups may serve as an *intra*molecular diluent reducing the polar interactions between polymer segments due to shielding. Thus, the local monomer concentration $c_{M,loc}$ in the vicinity of the propagating chain-end is closer to the overall monomer concentration $c_{M,a}$ in the system.

As currently there is no measure for $c_{M,loc}$, $k_{p,exp}$ data from PLP-SEC experiments are determined on the basis of the overall or bulk monomer concentration $c_{M,a}$. As long as the occurrence of $c_{M,loc}$ cannot be accounted for, an apparent $k_{p,exp}$ will be observed. If the ratio $c_{M,loc}/c_{M,a}$ is different for monomers with short ester groups and for monomers with long ester groups, the observed increase in $k_{p,exp}$ with ester size may - at least partly - reflect these differences. This idea is supported by experimental results from PLP-SEC bulk experiments of methacrylates with branched alkyl ester groups and methacrylates carrying a bulky ester groups.

Table 2: Propagation rate coefficients $k_{p,exp}$ for methacrylate homopolymerizations carried out in bulk at 50°C and ambient pressure. For details and references see text.

monomer	MMA	BMA	DMA	iDMA	EHMA	CHMA	BzMA	iBoMA
$k_{p,exp}$ ($L \cdot mol^{-1} \cdot s^{-1}$)	648	757	995	959	944	1257	1224	1002

The propagation rate coefficients for the dodecyl, *i*-decyl (iDMA), and the 2-ethylhexyl (EHMA) ester of the methacrylic acid are very close although the ester groups are different in size.[9] The propagation rate coefficients for these monomers obtained for bulk polymerizations at 50°C differ only by 5 % (see Table 2). Therefore, it may be concluded that all three ester groups result into a comparable situation in the vicinity of the propagating radical chain-end. Irrespective of the ester size, *intra*molecular interactions between polymer segments occur to a similar extent. This explanation agrees with the idea that the ester groups shield polar groups from each other. If the ester group reaches a certain length, the shielding does no longer depend on the actual size of the ester group. Branched ester groups will lead to a comparable extent of shielding.

For methacrylates carrying a cyclic ester group, such as cyclohexyl (CHMA) and benzyl methacrylate (BzMA) almost identical $k_{p,exp}$ are observed[30] (see Table 2). For *i*-bornyl methacrylate (iBoMA), a monomer with a very bulky ester group, a similar $k_{p,exp}$ for bulk polymerizations at 50°C is obtained (see Table 2).[30] In these cases the sterically hindered ester group with lower flexibility may be regarded as a spacer in-between the polymer segments, reducing the interactions between polar groups.

An increase of $k_{p,exp}$ with the size of the ester group is not only seen in methacrylate polymerizations. The variation of k_p with ester size is very similar within the family of

the acrylates and within the family of the methacrylates, which is reflected by the following ratios of $k_{p,exp}$ for the methyl, butyl, and dodecyl esters:

acrylates	$k_{p,exp}$(MA) : $k_{p,exp}$(BA) : $k_{p,exp}$(DA) = 1 : 1.2 : 1.5
methacrylates	$k_{p,exp}$(MMA) : $k_{p,exp}$(BMA) : $k_{p,exp}$(DMA) = 1 : 1.2 : 1.5

These ratios indicate that the variation of $k_{p,exp}$ with ester size within a monomer family is not affected by the different substituents at the double bond (H vs. CH_3). The surroundings of the propagating radical chain-end and thus $c_{M,loc}$ may be similarly affected by ester groups of the same size within the acrylate and within the methacrylate family.

Conclusions

The influence of fluid and supercritical CO_2 on the propagation kinetics in free-radical polymerizations may be explained considering local monomer concentrations. Variations in $c_{M,loc}$ are assumed to occur in systems where *intra*segmental interactions are operative and where the solvent quality of CO_2 (or of a conventional solvent) for the polymer differs significantly from the solvent quality of the monomer. Further, it is discussed that the occurrence of $c_{M,loc}$ may also - at least partly - explain the frequently observed increase of $k_{p,exp}$ with the initiating laser pulse repetition rate and the increase of $k_{p,exp}$ with ester size within the methacrylate and within the acrylate family. The findings suggest that the influence of CO_2 (or a conventional solvent), of the laser pulse repetition rate, and of the size of the ester group in the acrylate and in the methacrylate family are not intrinsic kinetic effects, but should at least partly be due to thermodynamic effects.

It should be mentioned that experimentally determined $k_{p,exp}$ data are very well suited for e.g. modeling of polymerization reactions, since the monomer concentrations used in these models are the overall monomer concentrations in the system, too. In addition, k_t data derived from the coupled parameter k_p/k_t should not significantly be influenced, since k_p/k_t is also derived using the overall monomer concentration.[34]

Acknowledgements

The author gratefully acknowledges financial support by the Deutsche Forschungsgemeinschaft and the Bundesministerium für Bildung und Forschung

[1] O. F. Olaj, I. Bitai, F. Hinkelmann, *Makromol. Chem.* **1987**, *188*, 1689

[2] O. F. Olaj, I. Schnöll-Bitai, *Eur. Polym. J.* **1989**, *25*, 635

[3] S. Beuermann, M. Buback, V. El Rezzi, M. Jürgens, D. Nelke, *in preparation for publication*

[4] S. Beuermann, M. Buback, T. P. Davis, R. G. Gilbert, R. A. Hutchinson, O. F. Olaj, G. T. Russell, J. Schweer, A. M. van Herk, *Macromol. Chem. Phys.* **1997**, *198*, 1545

[5] J. L. Kendall, D. A. Canelas, J. L. Young, J. M. DeSimone, *Chem. Rev.* **1999**, *99*, 543

[6] M. Buback, R. G. Gilbert, R. A. Hutchinson, B. Klumperman, F.-D. Kuchta, B. G. Manders, K. F. O'Driscoll, G. T. Russell, J. Schweer, *Macromol. Chem. Phys.* **1995**, *196*, 3267

[7] S. Beuermann, M. Buback, T. P. Davis, R. G. Gilbert, R. A. Hutchinson, A. Kajiwara, B. Klumperman, G. T. Russell, *Macromol. Chem. Phys.* **2000**, *201*, 1355

[8] M. Buback, C. H. Kurz, *Macromol. Chem. Phys.* **1998**, *199*, 2301

[9] R. A. Hutchinson, S. Beuermann, D. A. Paquet, Jr., J. H. McMinn, *Macromolecules* **1998**, *31*, 1542

[10] M. L. Coote, T. P. Davis, *Macromolecules* **1999**, *32*, 4290

[11] B. G. Manders, *PhD. Thesis*, University of Eindhoven, Eindhoven, The Netherlands, 1997

[12] M. Buback, C. H. Kurz, C. Schmaltz, *Macromol. Chem. Phys.* **1998**, *199*, 1721

[13] R. A. Lyons, J. Hutovic, M. C. Piton, D. I. Christie, P. A. Clay, B. G. Manders, S. H. Kable, R. G. Gilbert, *Macromolecules* **1996**, *29*, 1918

[14] S. Beuermann, D. A. Paquet, Jr., J. H. McMinn, R. A. Hutchinson, *Macromolecules* **1996**, *29*, 4206

[15] R. Balic, R. G. Gilbert, M. D. Zammit, T. P. Davis, C. Miller, *Macromolecules* **1997**, *30*, 3775

[16] R. A. Hutchinson, D. A. Paquet, Jr., J. H. McMinn, S. Beuermann, R. Fuller, C. Jackson, *5th International Workshop on Polymer Reaction Engineering* (DECHEMA Monographs 131), VCH Publishers, 467, 1995

[17] H. Y. Lachlan, M. L. Coote, P. C. Rodney, T. P. Davis, *J. Polym. Sci., Polym. Chem. Ed.* **2000**, *38*, 2192

[18] I. Popovic, S. Beuermann, M. Buback, *in preparation for publication*

[19] M. Buback, *Macromol. Symp.* **1996**, *111*, 229

[20] B. R. Morrison, M. C. Piton, M. A. Winnik, R. G. Gilbert, D. H. Napper, *Macromolecules* **1993**, *26*, 4368; S. Beuermann, M. Buback, G. T. Russell, *Macromol. Rapid Commun.* **1994**, *15*, 647; T. P. Davis, K. F. O'Driscoll, M. C. Piton, M. A. Winnik, *Macromolecules* **1989**, *22*, 2785; R. A. Hutchinson, J. R. Richards, M. T. Aronson, *Macromolecules* **1994**, *27*, 4530

[21] K. F. O'Driscoll, M. J. Monteiro, B. Klumperman, *J. Polym. Sci., Polym. Chem. Ed.* **1997**, *35*, 515; M. D. Zammit, T. P. Davis, G. D. Willett, K. F. O'Driscoll, *J. Polym. Sci., Polym. Chem. Ed.* **1997**, *35*, 2311

[22] S. Beuermann, M. Buback, C. Schmaltz , F.-D. Kuchta, *Macromol. Chem. Phys.* **1998**, *199*, 1209; C. Schmaltz, *PhD. Thesis*, Göttingen, 1998

[23] S. Beuermann, M. Buback, C. Schmaltz, *Macromolecules* **1998**, *31*, 8069

[24] S. Beuermann, M. Buback, C. Isemer, A. Wahl, I. Lacík, *Macromolecules*, submitted

[25] S. Beuermann, M. Buback, D. Nelke, *Macromolecules* **2001**, *34*, 6637

[26] F. Rindfleisch, T. P. DiNoia, M. A. McHugh, *J. Phys. Chem.* **1996**, *100*, 15581

[27] C. Isemer, *PhD. Thesis*, Göttingen, 2000

[28] S. I. Kuchanov, S. Russo, S. *Macromolecules* **1997**, *30*, 4511; P. Kratochvil, D. Straková, J. Stejskal, Z. Tuzar, *Macromolecules* **1983**, *16*, 1136

[29] H. I. Harwood, *Makromol. Chem., Macromol. Symp.* **1987**, *10/11*, 331; Y. D. Semchikov, *Macromol. Symp.* **1996**, *111*, 317

[30] R. A. Hutchinson, S. Beuermann, D. A. Paquet, Jr., J. H. McMinn, *Macromolecules* **1997**, *30*, 3490

[31] A. Wahl, *PhD. Thesis*, Göttingen, 1999

[32] A. M. v. Herk, B. G. Manders, D. A. Canelas, M. A. Quadir, J. M. DeSimone, *Macromolecules* **1997**, *30*, 4780

[33] O. F. Olaj, P. Vana, M. Zoder, A. Kornherr, G. Zifferer, *Macromol. Rapid Commun.* **2000**, *212*, 913

[34] S. Beuermann, M. Buback, C. Schmaltz, *Ind. Eng. Chem. Res.* **1999**, *38*, 3338