

## Initiation and Termination Kinetics in Fluid-Phase Free-Radical Polymerization up to High Pressure

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**Summary:** Rate coefficients of peroxyester decomposition in solution of *n*-heptane have been measured as a function of temperature and pressure. The data is used to determine initiator efficiencies for the ethene high-pressure polymerization. The efficiency strongly depends on the structure of the peroxyester. Free-radical termination rate coefficients of (meth)acrylate systems have been studied up to about 50 % monomer conversion. The reaction is controlled by segmental diffusion in the early period and by reaction diffusion at later stages of the polymerization.

### Introduction

Fluid phase free-radical polymerizations in extended ranges of pressure and temperature are of both fundamental and application-oriented interest. Of particular technical relevance are homo- and copolymerizations of ethene, carried out in *reactive* supercritical (sc) fluid phase, and polymerizations in *inert* sc fluid phase with carbon dioxide being the solvent medium in most cases. The benefits of polymerization under sc conditions - solvent and transport properties as well as concentrations and rate coefficients (and thus polymer properties) may be continuously tuned - are, however, countered by the unfavorable requirement of knowing reliable rate coefficients and phase behavior for a wide range of potential reaction conditions. Kinetic data is required for modeling and optimization of monomer conversion vs. time profiles and for estimates of polymer microstructure. As technical polymerization processes are mostly run up to higher degrees of monomer conversion, the variation of rate coefficients with conversion needs to be known, in addition to the pressure, temperature, and solvent dependence. This aspect is particularly important for diffusion-controlled reaction steps such as radical-radical termination, and also for initiation in which the primary free radical fragments from initiator decomposition need to get separated in order to independently start macromolecular growth. The first part of the paper addresses the temperature and pressure dependence of unimolecular decomposition rate coefficients of

alkyl peroxyesters in dilute solution of *n*-heptane. This rate data is used for the analysis of initiator efficiency of these peroxyesters in high-pressure ethene polymerization. The second part of the paper focuses on termination rate in free-radical homo- and copolymerizations carried out in extended regions of pressure, temperature, and conversion. These investigations are based on laser SP–PLP (single pulse–pulsed laser polymerization) experiments. This type of experiment is perfectly suited for studying detailed aspects of termination rate, including chain-length dependent termination.

## Experimental

Peroxide decomposition studies were carried out under turbulent flow conditions in a tubular reactor of 10 m length and 0.5 mm internal diameter. The experimental set-up and procedure have already been described.<sup>[1,2]</sup> High-purity peroxides were prepared and kindly supplied by AKZO NOBEL. Initial peroxide concentrations were 0.01 molar in *n*-heptane. Decomposition was studied up to 190°C and 2500 bar at residence times between 20 and 125 s. Peroxide concentration, after penetrating the tubular reactor, was measured IR-spectroscopically in an optical flow-through cell which is positioned directly behind the reactor and is fixed in the sample compartment of a Fourier-transform instrument (BRUKER IFS 88).

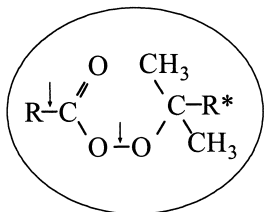
Initiator efficiencies of the peroxides (mostly aliphatic alkyl peroxyesters) were measured for ethene polymerizations at 2000 bar and temperatures between 150 and 250°C in a continuously operated mini-plant with a stirred tank reactor (CSTR). Details of the experimental set-up and of the procedure are presented elsewhere.<sup>[3,4,5]</sup>

Termination rate coefficients,  $k_t$ , are obtained from SP–PLP experiments in which polymerization induced by a single pulse (SP) of about 20 ns width is spectroscopically measured at around 6170 cm<sup>-1</sup> with a time resolution of a few microseconds. Fitting of the obtained monomer conversion vs. time traces yields  $k_t/k_p$ , the ratio of termination to propagation rate coefficients. With  $k_p$  being known from independent PLP–SEC (size-exclusion chromatography) experiments,  $k_t/k_p$  provides immediate access to  $k_t$ . The principal components of the SP–PLP experiment are an excimer laser, a stable tungsten halogen lamp, a monochromator, and a fast near infrared (NIR) detector of 2 μs time resolution. The set-up and experimental procedure are described in more detail elsewhere.<sup>[6,7]</sup> The monomers under investigation are: methyl acrylate (acrylic acid methyl ester (MA), Fluka, 99 %), butyl acrylate (BA, >99 %, Fluka), dodecyl acrylate

(DA, Fluka) which actually is a mixture of 55 % DA and 45 % tetradecyl acrylate, and dodecyl methacrylate (DMA, 99 %, Fluka). 2,2-dimethoxy-2-phenylacetophenone (DMPA, Aldrich, 99 %) was used as the photoinitiator in most of the SP-PLP experiments.

### **Decomposition rate and initiator efficiency of aliphatic peroxyesters**

Precisely knowing initiator decomposition rate coefficients,  $k_d$ , is required for simulation of polymerization processes. As it is the amount of primary free radicals which goes into the modeling, in addition the initiator efficiency,  $f$ , for polymerization of a particular monomer under given reaction conditions needs to be known.  $f$  is defined as the fraction of primary free radicals (from initiator decomposition) which starts monomer addition. The efficiency  $f$  is thus related to a maximum concentration of primary radicals that may be estimated from twice the amount of initiator decomposed. It should be noted that each number of  $f$  should be accompanied by the reference  $k_d$  value or it should be made clear which  $k_d$  value has been introduced into the estimate of initiator efficiency. With the product  $k_d f$  being the relevant quantity for characterizing the availability of primary growing radicals, it is easily understood that the determination of  $k_d$  values should be carried out under conditions which are as close as possible to the situation met during actual polymerization. In what follows, initiator efficiency of a series of aliphatic peroxyesters (POEs) in ethene high-pressure polymerization is discussed. Independent determinations of  $k_d$  have been performed on the POEs in dilute solution of *n*-hexane, considered to provide a molecular environment sufficiently close to the situation in ethene-polyethylene mixtures at typical polymerization conditions. High-pressure ethene polymerization is the archetype of free-radical polymerization processes carried out in supercritical fluid phase with the reaction conditions, however, being in both pressure and temperature far above the critical parameters of the ethene monomer. Despite the rather extreme reaction conditions, ethene high-pressure polymerization continues to be a large-scale process of eminent industrial importance. At polymerization temperatures and pressures up to 300°C and 3000 bar, respectively, the interest in carrying out extended sets of experimental studies for optimizing this reaction and for elucidating polymerization conditions under which special grades may be produced for obvious reasons is rather limited. Simulation procedures thus are highly advantageous in that they allow significant reduction of the number of experimental investigations.



Scheme 1.  
Structure of alkyl peroxyesters

$k_d$  has been studied for a series of aliphatic peroxyesters. Scheme 1 shows the general structure of POEs. The kinetic data is derived from spectroscopic determination of peroxide content after passing a tubular reactor at a series of precisely known reactor residence times. With the exception of studies into formates ( $R = H$ ) carried out by Hinrichs,<sup>[8]</sup> the  $R$  substituent on the „acid side“ of the POE was an alkyl group with the C-atom positioned next to the carbonyl moiety being either primary (including acetates,  $R = CH_3$ ), secondary or tertiary. The  $R^*$  substituent on the alcohol side mostly was  $CH_3$  (*tert*-butyl POEs),<sup>[2,9]</sup> but also was  $C_2H_5$  (*tert*-amyl POEs),  $CH_2$ -*tert*-butyl (tetramethyl butyl POEs), or *tert*-butyl (tetramethyl propyl POEs).

For the entire series of POE decomposition studies in *n*-heptane solution at initial peroxide concentrations of 0.01 molar, the decomposition rate follows first-order kinetics over at least two reaction half-lives. The observed first-order rate coefficients,  $k_d$ , may however be composed of several elementary reaction steps such as dissociation, recombination, out-of-cage diffusion, and fast consecutive reaction steps of primary intermediates.<sup>[9]</sup> Thus the  $k_d$  values should be addressed as „overall first-order decomposition rate coefficients“. Variation of the  $R^*$  substituent results in only a minor effect on  $k_d$ . On the other hand, modification of the  $R$  substituent on the „acid side“ of the POEs may enormously vary  $k_d$ . Strong effects are seen upon variation of the type of  $\alpha$ -carbon atom in  $R$  from primary to secondary and to tertiary as is illustrated by Arrhenius plots of experimental  $k_d$  data for *tert*-butyl peroxyformate (TBPF), *tert*-butyl peroxy-*n*-pentanoate (TBPnP), *tert*-butyl peroxy-2-ethylhexanoate (TBPEH), and *tert*-butyl peroxy-pivalate (TBPP) in Figure 1. The data sets have been taken at different pressures: TBPF and TBPnP at 500 bar,<sup>[8]</sup> TBPEH at 1000 bar,<sup>[9]</sup> and TBPP at 2000 bar.<sup>[2]</sup> The pressure effect on  $k_d$  is very small as compared to the variation with temperature. Thus plotting  $k_d$  of the four peroxyesters for identical pressure, with the required data being easily available from the fitted equations for  $k_d(p,T)$ ,<sup>[8,9]</sup> will not affect the message contained in Figure 1. At constant temperature,  $k_d$  increases in steps

of approximately one order of magnitude in going from TBPf to the „primary“ peroxyester TBPnP, to the „secondary“ peroxyester TBPEH, and to the „tertiary“ peroxyester TBPP. The POEs depicted in Figure 1 thus allow for free-radical production within a very extended region of temperatures.

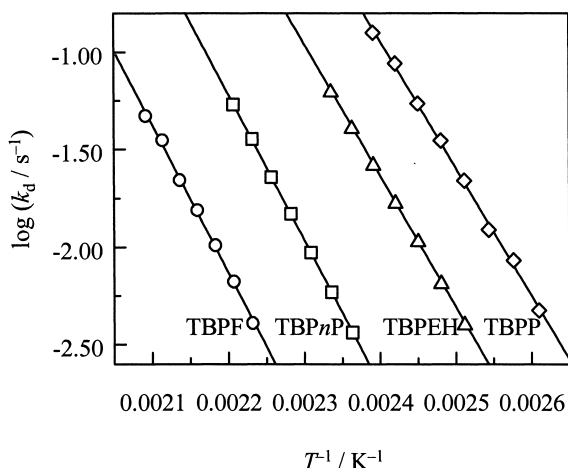


Figure 1. Temperature dependence of the first-order decomposition rate coefficient of several peroxyesters measured in dilute solution of *n*-heptane. The pressures are 500 bar for *tert*-butyl peroxyformate (TBPf) and *tert*-butyl peroxy-*n*-pentanoate (TBPnP) and are 1000 bar for *tert*-butyl peroxy-2-ethylhexanoate (TBPEH) and 2000 bar for *tert*-butyl peroxy-pivalate (TBPP).

Analysis of the  $k_d$  data as a function of temperature and pressure for an extended series of POEs <sup>[2,9]</sup> including the ones contained in Figure 1 clearly suggests that the formates, acetates and the entire set of „primary“ POEs, such as TBPnP, undergo only O–O bond scission in the primary dissociation step to yield an acyloxy and an alkyloxy radical whereas the „secondary“ and „tertiary“ POEs exhibit concerted two-bond scission associated with the instantaneous production of CO<sub>2</sub> and of a carbon-centered alkyl radical (together with the alkyloxy radical). It should be noted that, in addition to the differences in decomposition rate, the type of primary free radicals, oxygen-centered or carbon-centered, may be relevant as these two types of free-radicals significantly differ in chain-transfer activity. The type of primary free radicals should be of particular importance for potential in-cage reactions and thus for initiator efficiency. It should also be mentioned that variation of R\* may affect the type of caged free radicals. For example, (carbon-centered) *tert*-butyl radicals may be very rapidly produced under in-cage conditions (together with acetone) during tetramethylpropyl POE decomposition by  $\beta$ -scission of primary tetramethylpropyloxy radicals. The (oxygen-centered) *tert*-butoxy radical which is produced in the decomposition of the *tert*-butyl POEs contained in Figure 1 will not easily undergo such a consecutive reaction.

Plotted in Figure 2 are the initiator efficiencies in ethene polymerization at 2000 bar of the peroxyesters TBPnP,<sup>[8]</sup> TBPEH and TBPP.<sup>[3,4,10]</sup>  $k_d$  data for these peroxides were presented in Figure 1. TBPF, for which  $k_d$  data were also contained in Figure 1 has not yet been subjected to detailed efficiency studies as the molecule seems to be vulnerable to some catalyzed decomposition at rather low temperature.

The procedure of carrying out the peroxyester-initiated high-pressure ethene polymerizations and of deducing initiator efficiency,  $f$ , from the experimental data is presented in detail elsewhere.<sup>[3,4,10]</sup> The estimate of  $f$  proceeds via Eq. (1):

$$f = \left( \frac{\Delta X_r}{1 - \Delta X_r} \right)^2 \cdot \frac{k_t}{(\tau \cdot k_p)^2} \cdot \frac{\rho_{in}}{\rho_{out} \cdot c_{INI,0}} \cdot \frac{1 + \tau \cdot k_d}{k_d} \quad (1)$$

where  $\Delta X_r$  is the peroxide-induced ethene conversion,  $\rho_{in}$  and  $\rho_{out}$  are the densities of the reaction mixture which enters ( $\rho_{in}$ ) and exits ( $\rho_{out}$ ) the CSTR,  $\tau$  is residence time (in the CSTR),  $c_{INI,0}$  is the peroxide concentration fed into the CSTR, and  $k_t$ ,  $k_p$ , and  $k_d$  are the ethene termination and propagation rate coefficients and the peroxide decomposition rate coefficient, respectively. These rate coefficients refer to the actual polymerization conditions. The important point to note is that  $k_t$ ,  $k_p$ , and  $k_d$  are taken from three independent experiments. These rate coefficients are used as derived from the separate experiments with only  $k_t$  requiring some minor adjustment for the conversion dependence of this diffusion-controlled rate coefficient.<sup>[10]</sup> It is gratifying to see that the resulting  $f$  values are of reasonable size. They are considered to be accurate within  $\pm 15$  %. It should be noted that initiator efficiencies measured for di-*tert*-butyl peroxide with the same apparatus and according to the same evaluation procedure are close to unity<sup>[3,4]</sup> which fully meets the expectation and thus provides strong evidence for the experimental method and the mode of analysis being highly appropriate which should also be true for the kinetic analyses used within the independent determinations of  $k_t$ ,  $k_p$ , and  $k_d$ . Among this data, it is particularly noteworthy that the quality of the ethene  $k_t$  values deduced via the SP–PLP technique by Schweer<sup>[11]</sup> is high. The reported data for ethene conversions around 4.5 per cent which are typical for the peroxide-induced ethene polymerizations yield, without any modification,  $f$  values as shown in Figure 2.

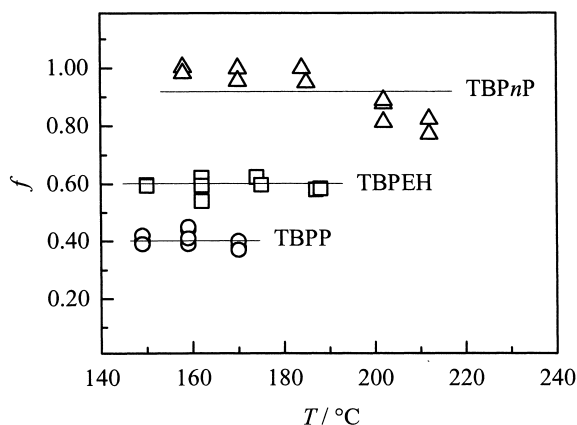
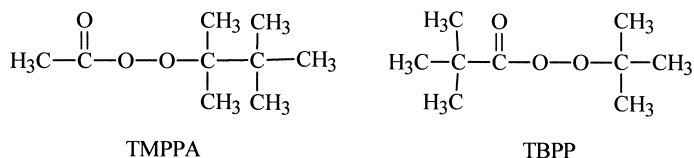


Figure 2. Initiator efficiency of *tert*-butyl peroxy-*n*-pentanoate (TBPnP), *tert*-butylperoxy-2-ethyl-hexanoate (TBPEH), and *tert*-butyl peroxy-pivalate (TBPP) in ethene homopolymerization at 2000 bar and several temperatures.

The efficiencies are clearly different for the three peroxyesters. For the „primary“ one, TBPnP,  $f$  is close to unity with this value being slightly reduced toward higher temperature. It is not yet fully clear whether this decrease is of kinetic origin or whether it reflects incomplete initiator mixing into the CSTR which will be associated with some reduction in  $f$ . The efficiencies of the „secondary“ and of the „tertiary“ peroxyesters are significantly lower:  $f_{\text{TBPEH}}$  is around 0.6 and  $f_{\text{TBPP}}$  is close to 0.4. The primary reason behind these differences is seen in the extent of in-cage cross-disproportionation. An important such disproportionation reaction is the one between the *tert*-butoxy radical and a carbon-centered free radical with one (or more) abstractable hydrogen atom(s) in  $\beta$ -position to the radical functionality. There are nine such H-atoms on the *tert*-butyl radical which is instantaneously available in TBPP decomposition occurring via concerted two-bond scission. The lowering of  $f$  associated with cross-disproportionation thus will be particularly pronounced with TBPP. The opposite is true for „primary“ *tert*-butyl peroxyesters, such as TBPnP. As is known from the peroxide decomposition studies in *n*-heptane solution<sup>[2,9]</sup> (and see above), single-bond scission occurs in the primary kinetic event which yields an acyloxy radical (plus the *tert*-butoxy radical). The acyloxy radical has no such H-atom in  $\beta$ -position to the radical functionality and thus will not readily undergo cross-disproportionation unless a suitable carbon-centered radical is formed by subsequent decarboxylation. This reaction, however, takes place on a time scale which exceeds the life-time of the caged species. The two primary radicals from TBPnP decomposition, of course, may recombine to yield the peroxide back which has the chance to re-dissociate into free radicals that can successfully initiate polymerization during a subsequent dissociation event, perhaps after several

dissociation-recombination cycles. Recombination of the primary radicals from TBP $n$ P decomposition does not affect  $f$ , as this cage process, to a similar extent, should also occur during peroxyester decomposition in *n*-heptane (in the absence of any polymerizable monomer). The process thus is already contained in the  $k_d$  value which goes into the estimate of  $f$  via Eq. (1). In the absence of cross-disproportionation or with this reaction being of minor importance,  $f$  should be close to unity. This is indeed what is found in ethene polymerizations induced by TBP $n$ P<sup>[8]</sup> and also by the other „primary“ peroxyesters studied so far.<sup>[3,4,10]</sup> Also for di-*tert*-butyl peroxide where the two primary *tert*-butoxy radicals will not readily undergo cross-disproportionation,  $f$  is close to unity, as has already been mentioned.<sup>[3,4]</sup> That in-cage cross-disproportionation between an oxygen-centered radical and a carbon-centered radical with at least one H-atom in  $\beta$ -position has a major impact on  $f$ , can also be seen from the initiator efficiency being low and being approximately the same, between  $f = 0.4$  and  $f = 0.5$ , for TBPP and for tetramethyl-propyl peracetate (TMPPA). The two components are shown in Scheme 2.



Scheme 2.

As is easily seen, TMPPA leads to in-cage production of the oxygen-centered free radical  $\text{CH}_3\text{C}(\text{O})\text{O}\cdot$ , which occurs as a consequence of O–O single-bond scission of this „primary“ peroxyester. The second in-cage free radical product will be the *tert*-butyl radical which is immediately formed by  $\beta$ -scission of the tetramethylpropyloxy radical. The latter reaction occurs extremely fast. The interesting observation with the two peroxyesters in Scheme 2 is that the carbon-centered *tert*-butyl radical and also the oxygen-centered radical may be produced either from the „acid side“ or from the „alcohol side“ of the POE. If both species are becoming available under in-cage conditions, the cross-disproportionation reaction will take place and, as a consequence, the initiator efficiency will be reduced.

The „secondary“ peroxyester in Figure 2 (TBPEH) shows an intermediate type of behavior. Within forthcoming studies, the correlation of  $f$  with the type and with the time scale of availability of in-cage free radicals will be addressed in some more detail,



as will be the diffusivity of the primary radical species. Studies into tertamethylpropyl peroxyvalate appear to be of particular interest as two *tert*-butyl radicals will be available under in-cage conditions, which may not be sufficiently reactive to undergo cross-disproportionation but may recombine before leaving the cage. It remains also to be studied whether and to which extent initiator efficiency is lowered toward higher degrees of monomer conversion. The discussion so far assumes  $f$  to be essentially controlled by in-cage processes and that escaping cross-disproportionation (and in-cage recombination) before leaving the cage is equivalent to successful reaction with the monomer outside the cage. This simplifying picture may require some modification at very high bulk viscosities associated with high polymer contents. Nevertheless, the results presented in Figures 1 and 2 appear to be very helpful for the design and for the proper selection of peroxyester initiators.

### **Free-radical termination rate in compressed fluid phase**

Termination of free radicals proceeds via combination or via disproportionation which two reaction steps are also involved in initiation kinetics (see above). In spite of this similarity, termination is significantly more difficult to understand than is initiation and no generally accepted model for homo- and copolymerization termination kinetics in extended regions of pressure, temperature, and conversion has emerged so far. The complexity of free-radical termination kinetics results from the fact that for this process to occur several consecutive elementary reaction steps have to take place. The two radicals need to approach each other, by either translational diffusion or by reaction diffusion.<sup>[12]</sup> After getting overlapped, the two radicals have to explore a multitude of conformations to reach a sufficiently close proximity of the two free-radical sites for the (final) combination or disproportionation step to occur. The overall process, which is generally considered to be diffusion controlled, combines physical dynamics, such as the diffusivity of the entire free radical and/or of segments of the macroradical, with chemical reactivity. The complexity of the problem results from the broad size distribution of both free radicals and of (dead) polymer molecules which occur in conventional free-radical polymerization. Both distributions may significantly affect physical dynamics. The detailed analysis of termination rate should also consider effects resulting from the branching structure of macroradicals and of polymer molecules. Further difficulties arise due to the enormous increase in viscosity during polymerization, e.g., by several orders of magnitude in bulk polymerizations. As a

consequence, several modes of termination mechanism may be operative during reaction up to high conversion. Size distribution and branching of macroradicals and (thus) of polymer may strongly depend on the selection of initial reaction conditions and on the mode of carrying out a specific polymerization. It is primarily because of diffusion-controlled termination that free-radical polymerization kinetics and product properties depend on the history of each particular polymerization process.<sup>[13]</sup>

With all this complexity in mind, any attempt to describe termination kinetics in detail appears to be beyond reach. Each number for  $k_t$  should be accompanied by an extended list of additional information, e.g., on size and branching distributions of radicals and of polymer molecules, on bulk viscosities (diffusivities) and on segment mobilities with all this data referring to the actual polymerization conditions for which  $k_t$  has been measured. It is gratifying to note that this unfavorable and difficult situation is not all-invasive. Thus polymerization conditions have been identified under which the dependence of termination rate on free-radical chain length is not very pronounced. Moreover, conversion regions have been found in which the dependence of termination rate on monomer conversion is weak or may even not be detectable. A few examples of such simple types of conversion dependence of termination will be presented in the remaining part of this paper.

The SP-PLP experiment is perfectly suited for mapping out the dependence of termination rate on overall monomer conversion and, simultaneously, for providing information that concerns the chain-length dependence (CLD) of  $k_t$ . The termination rate coefficient is deduced from laser-induced monomer conversion which is measured spectroscopically on a  $\mu\text{s}$  time scale. The conversion per pulse mostly does not exceed 1 % and is typically of the order of 0.1 % or even below. Thus a series of such SP-PLP experiments may be carried out during a polymerization reaction up to high overall conversion  $X$  with the  $k_t$  values from each SP-PLP experiment referring to a narrow range of monomer conversion. Within each individual SP-PLP experiment, the chain length is linearly correlated with time  $t$  after applying the UV excimer laser pulse of about 20 ns width. Unless chain transfer processes come into play, at any time  $t$ , termination occurs between two radicals of almost identical chain length. As a consequence, analysis of different time regions of the laser-induced monomer conversion vs.  $t$  (SP-PLP) trace may provide information about the CLD of  $k_t$ . This latter aspect has been studied in detail for styrene, methyl methacrylate and several

acrylates in the initial polymerization period where relatively weak, but clearly detectable chain-length dependences have been obtained.<sup>[14]</sup> The results are in good agreement with data reported by Olaj and Vana,<sup>[15]</sup> by Mahabadi,<sup>[16]</sup> and by de Kock,<sup>[17]</sup> who used different procedures. In what follows, only the dependence of termination rate on overall monomer conversion,  $X$ , will be addressed. The  $k_t$  data reported for any given value of  $X$  should be referred to as chain-length averaged termination rate coefficients.

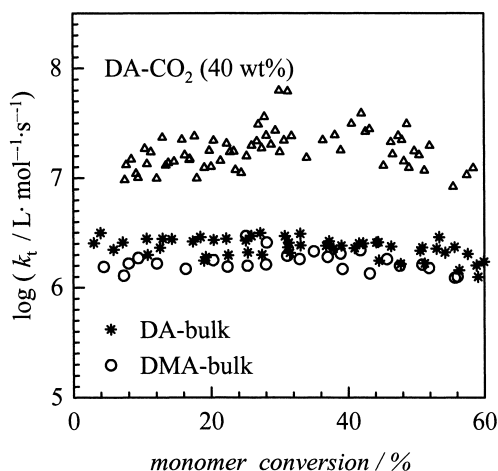


Figure 3. Homopolymerization  $k_t$  as a function of monomer conversion (in %) for free-radical bulk polymerizations of dodecyl acrylate (DA) and dodecyl methacrylate (DMA) and of DA in solution containing approximately 40 wt.%  $\text{CO}_2$ . All data refer to 40°C and 1000 bar.

Shown in Figure 3 are  $k_t$  data from SP-PLP experiments on dodecyl acrylate (DA) and dodecyl methacrylate (DMA) homopolymerizations<sup>[18]</sup> and on DA homopolymerization in solution containing approximately 40 wt.-%  $\text{CO}_2$ .<sup>[19]</sup> The entire set of  $k_t$  data has been determined at 40°C and 1000 bar. The most remarkable observation from Figure 3 is that  $k_t$  remains constant during DA and DMA bulk homopolymerizations up to about 50 % monomer conversion, even though bulk viscosity increases, by several orders of magnitude, with the viscosity vs. conversion correlation, however, not yet being quantitatively known. Whereas the enormous change in viscosity during bulk homopolymerization is not reflected in  $k_t$ , addition of 40 wt.-%  $\text{CO}_2$  to DA is associated with a clearly enhanced  $k_t$  value which is by almost one order of magnitude above bulk  $k_t$ . The plateau behavior of  $k_t$  observed within each of the polymerizations (Figure 3) strongly suggests that termination is controlled by segmental diffusion. The formation of an overlapping pair of free radicals by center-of-mass diffusion, which has to precede segmental reorientation of the chain ends, does not appear to be rate determining as  $k_t$  is insensitive toward bulk viscosity. The initial polymerization range in which  $k_t$  is more or

less constant (Figure 3) may be fairly extended, e.g. with monomers such as DA and DMA, but extends only up to about 10 to 20 % in case of methyl acrylate (MA) and methyl methacrylate (MMA) bulk homopolymerizations.<sup>[18,20]</sup> Segmental reorientation of the overlapping chains takes place in the intra-coil surroundings which is primarily made up of the monomer (or of the monomer-solvent mixture in case of solution polymerizations). For solution polymerizations of MMA, Fischer et al.<sup>[21]</sup> demonstrated that  $k_t$  scales with the inverse of solution viscosity with the latter quantity being determined on the monomer-solvent mixture *prior* to polymerization. The plateau region of homopolymerization  $k_t$  thus is understood as being due to a single type of segment diffusing within the same intra-coil surroundings made up primarily of the monomer or of a monomer-solvent mixture. This argument is strongly supported by the finding that the plateau  $k_t(p,T)$  values in styrene bulk homopolymerization scale with the inverse of styrene (monomer) viscosity,  $\eta(p,T)$ .<sup>[22]</sup> It should be noted that the important contribution to low conversion  $k_t$  of segmental diffusion has early been highlighted by O'Driscoll and Mahabadi.<sup>[23]</sup> These authors report that, in addition to segmental friction, changes in polymer coil dimension resulting from solvent quality may contribute to segmental diffusion. These additional thermodynamic-type effects may even give rise to an *increase* in  $k_t$  with monomer conversion,  $X$ , during the early polymerization period. They may vary with temperature and with pressure.<sup>[24]</sup> A pronounced increase of  $k_t$  with  $X$  has been found in butyl acrylate polymerization in supercritical CO<sub>2</sub>.<sup>[25]</sup> Within a detailed analysis of  $k_t$  at low and moderate conversion, modifications of segment surroundings associated with changes in polymer concentration need to be considered. In solution polymerizations changes in monomer-to-solvent concentration ratio during reaction have to be taken into account.

Intra-coil mobility is, however, not the only one property which controls  $k_t$  in the segmental diffusion regime. This is suggested by differences in plateau  $k_t$  values of monomers not being correlated with the associated differences in monomer viscosity. Steric hindrance at the free-radical site appears to significantly affect  $k_t$ . This entropic contribution has been studied for copolymerizations of acrylate monomers, e.g. for the MA-DA system, in quite some detail.<sup>[18]</sup> Among the existing models for copolymerization  $k_t$  only the one which considers terminal and penultimate units at the free-radical terminus and uses the geometric mean approximation to estimate (penultimate) cross-termination rate coefficients is capable of adequately representing

experimental  $k_{t, \text{copo}}$  data. The underlying model is based on the assumption of steric hindrance being termination rate controlling.<sup>[26]</sup> The consideration (only) of terminal and penultimate units at both free-radical chain ends appears to adequately take most of this shielding effect on  $k_t$  into account. The importance of shielding is also suggested by the plateau  $k_t$  values of DA and DMA being more or less the same, as is shown in Figure 3. The long ester tail (on the terminal and penultimate units of free radicals in both DA and DMA) reduces the probability of immediate termination occurring once the radical chain ends are in close proximity. The dodecyl ester group thus makes a significant fraction of the encounter processes unsuccessful with respect to termination. The chain ends may diffuse apart before combination or disproportionation has taken place. Addition of CO<sub>2</sub> (Figure 3) goes with a significant lowering of intra-coil monomer–solvent viscosity. As a consequence, segmental reorientation is speeded up. The associated increase in the number of chain-end encounters enhances the probability of termination and thus enhances  $k_t$ . These arguments are consistent with  $k_t$  data measured for MA and MMA.<sup>[18]</sup> Addition of an  $\alpha$ -methyl group in going from MA to MMA significantly changes the steric situation and lowers  $k_t$  whereas upon going from DA to DMA the additional  $\alpha$ -methyl group induces no change in  $k_t$  because of the dominant contribution to  $k_t$  of the long alkyl ester chain. The poor shielding situation with MA is associated with a high fraction of chain-end encounters leading to termination. As a consequence, further enhancement of segmental mobility, e.g., by adding CO<sub>2</sub>, does not result in any pronounced enhancement of  $k_t$ .

Among the systems studied so far a significant number of homo- and copolymerization systems has been found which exhibit a fairly extended plateau region of almost constant  $k_t$  in the initial polymerization period. This observation is extremely helpful for modeling purposes. Toward higher degrees of monomer conversion,  $k_t$  may significantly drop, as is particularly well-known for methyl methacrylate bulk polymerization. In the gel effect region,  $k_t$  decreases by orders of magnitude as a consequence of an enormous reduction in center-of-mass diffusivity. Bulk viscosity may increase to such an extent that translational diffusion of free radicals is suppressed. Under these conditions, termination may proceed via “reaction diffusion” according to which mechanism free-radical sites may approach each other by a sequence of propagation steps in conjunction with segmental mobility of the chain ends.<sup>[12,27]</sup> In case of reaction diffusion being termination rate controlling, the associated rate coefficient,  $k_{t, \text{RD}}$ , should be proportional

to the propagation rate coefficient,  $k_p$ , and to the actual monomer concentration,  $c_M$ :  $k_{t,RD} = \text{constant} \cdot k_p \cdot c_M$ , which may be rewritten:

$$k_{t,RD} = C_{RD} \cdot k_p \cdot (1 - X) \quad (2)$$

where  $C_{RD}$  is the reaction-diffusion constant. If  $C_{RD}$  is independent of conversion and is rather similar for a family of monomers, e.g., for the alkyl acrylates,  $k_{t,RD}$  should not be too different for the individual members of this family.

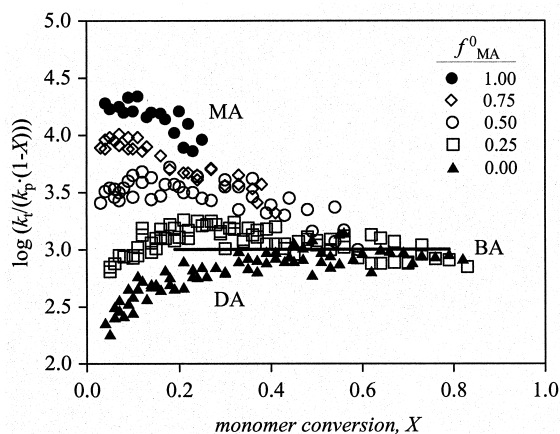


Figure 4. Conversion dependence of the term  $k_t/(k_p \cdot (1-X))$  of MA and DA homo- and copolymerizations and of BA homopolymerization (full line) at low pressure. The reaction conditions are 30°C/10 bar for the MA-DA systems and are 70°C and ambient pressure for BA homopolymerization.

Plotted in Figure 4 is  $\log(k_t/(k_p \cdot (1-X)))$  for several low pressure free-radical homopolymerizations of MA, BA, and DA and for three MA-DA copolymerizations at MA monomer mole fractions of  $f_{MA} = 0.25, 0.50$ , and  $0.75$ .<sup>[28]</sup> The temperature and pressure conditions of the MA and DA homo- and copolymerizations were 30°C and 10 bar. The BA data which shows no conversion dependence at  $X > 0.2$  (that is above 20 %) refers to 70°C and ambient pressure.<sup>[29]</sup> According to Eq. (2), the expression  $k_t/(k_p \cdot (1-X))$  should equal  $C_{RD}$  under conditions where termination is controlled by reaction diffusion:  $k_t = k_{t,RD}$ . Interestingly,  $k_t/(k_p \cdot (1-X))$  is very different for MA and DA homopolymerizations at low conversion. This comes as no surprise because termination is assigned to segmental diffusion control in the initial polymerization region. At about 20 % conversion,  $k_t$  of MA starts to significantly decrease.<sup>[28]</sup> This change can also be seen from the  $k_t/(k_p \cdot (1-X))$  data for MA in Figure 4. The same trend is seen with the MA-rich copolymerizations. At high conversions, e.g., above 50 %, the  $k_t/(k_p \cdot (1-X))$  data of the MA and DA homo- and copolymerizations seem to be very close to each other and are close to the corresponding BA value represented by the straight line. In

this high conversion range, reaction diffusion is assumed to control  $k_t$ . Under reaction diffusion conditions a single  $C_{RD}$  value allows to estimate  $k_t$ . With BA, this range is fairly extended whereas, with DA, reaction diffusion control appears to be approached (from lower  $k_t/(k_p(1-X))$  only at high conversion.  $C_{RD}$  seems to be insensitive toward the moderate difference in temperature, 30 vs. 70°C, which is in agreement with earlier findings of Huckestein.<sup>[30]</sup> The reason behind the remarkable constancy of  $C_{RD}$  for the series of alkyl acrylates is seen in  $C_{RD}$  being associated with chain flexibility which should be similar for the members of the alkyl acrylate family. It goes without saying that  $C_{RD}$  being a “good constant” should be extremely useful for modeling free-radical polymerization at moderate and high conversion. Although the trends of conversion dependence of  $k_t$  are becoming clear, further studies, including separate investigations into the dynamics of polymer solutions, need to be carried out. Each mode of diffusion control, moreover, should be associated with a characteristic type of chain-length dependence of  $k_t$ . Such aspects are currently under investigation in our laboratory.

## Conclusion

Accurate kinetic studies into the decomposition rate of peroxides in dilute solution carried out in conjunction with the measurement of peroxide-induced monomer conversion in a continuously operated stirred tank reactor allow for the determination of initiator efficiency,  $f$ , under fluid phase conditions up to high pressure and temperature. In ethene high-pressure polymerizations initiated by alkyl peroxyesters a major impact of peroxide structure on  $f$  is seen. A strong reduction in  $f$  is associated with the in-cage recombination of an oxygen-centered radical with a carbon-centered radical bearing at least one hydrogen atom in  $\beta$ -position to the radical site.

Termination rate, in general, is difficult to be adequately described as polymer content and also the size of free radicals and of polymer molecules affect the physical dynamics. Studies into (meth)acrylates demonstrate that in conversion regions where segmental diffusion (SD) or reaction diffusion (RD) control the termination process, representation of the  $k_t$  behavior appears not to be overly complicated. With several monomers, plateau values of  $k_{t,SD}$  have been observed over fairly extended regions of monomer conversion,  $X$ . The variation of  $k_{t,RD}$  is correlated with  $X$  and may be modeled at known propagation rate by using the reaction diffusion constant,  $C_{RD}$ , as the only one additional parameter.  $C_{RD}$  appears to be very similar for monomers belonging to the same family as is indicated by the alkyl acrylate data.

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