Macromolecules **1999,** *32,* 1445−1452

Termination Kinetics in Free-Radical Bulk Copolymerization: The Systems Dodecyl Acrylate−Dodecyl Methacrylate and Dodecyl Acrylate−Methyl Acrylate

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Received September 18, 1998; Revised Manuscript Received December 30, 1998

ABSTRACT: The termination kinetics in free-radical bulk copolymerization of the dodecyl acrylate (DA)−dodecyl methacrylate (DMA) and DA−methyl acrylate (MA) systems has been studied by exclusively applying laser-assisted techniques. The ratio of termination to propagation rate coefficients, k_t/k_p, is measured by the SP−PLP technique, and k_p is deduced from PLP−SEC. k_t is determined up to fairly large degrees of overall monomer conversion, at least up to 40%. The discussion of the present paper focuses on the initial plateau region of constant k_t, which extends up to about 15% in MA homopolymerizations and up to 70% in DA homopolymerizations. Among the existing models for copolymerization k_t, the treatment that considers penultimate units and uses the geometric mean approximation to estimate cross-termination turns out to be excellently applicable. It is particularly noteworthy that plotting log k_t vs monomer mole fraction (f_i) yields a linear correlation for each of the two copolymerization systems. The excellent fit of $k_{t,\text{copo}}$ by the penultimate unit model provides some evidence that steric effects significantly contribute to termination rate control in (meth)acrylate free-radical polymerization at low and moderate degrees of monomer conversion. The entire set of experiments has been carried out at high pressure (1000 bar, 40 °C) where the signal-to-noise ratio of the SP−PLP experiments is very satisfactory. No reason is seen why the conclusions derived from these measurements should not be valid at other reaction conditions including ambient pressure.

Introduction

The introduction of laser-assisted techniques has enormously improved the quality of rate coefficient measurements in free-radical polymerization.[1] Pulsed-laser polymerization (PLP) using sequences of evenly spaced pulses in conjunction with subsequent size-exclusion chromatographic (SEC) analysis of the resulting polymer, as first used by Olaj and his group,[2] has become the preferred method for accurate determination of propagation rate coefficients, k_p. Data derived by this PLP−SEC technique has been used by the IUPAC Working Party "Modeling of Polymerisation Kinetics and Processes" to collate benchmark k_p values for styrene[3] and for methyl methacrylate.[4] Corresponding work on a wide variety of monomers is in progress as are studies into copolymerization k_p.[5] Applying PLP in conjunction with online spectroscopic detection of monomer conversion allows for the measurement of termination rate coefficients, k_t, by directly determining k_p/k_t and by taking k_p from PLP−SEC. Near-infrared spectroscopy has mostly been used for such online quantitative analysis of monomer conversion induced either by a single laser pulse (SP−PLP)[6] or by pulse sequences (PS−PLP).[7,8] The SP−PLP experiment in which polymerization induced by a single pulse of about 20 ns width is measured with a time resolution of microseconds constitutes a particularly powerful method for k_t determination. The applicability of the method could recently be extended to investigations into monomers that are high in k_t and low in k_p, such as methyl methacrylate.[9] Under such conditions, high k_t and low k_p, polymerization induced by a single pulse is rather small which results in a reduced signal-to-noise of the measured conversion vs time (after the pulse) trace and thus in enlarged uncertainties of the k_t data. This problem may be overcome by co-adding numerous (typically up to 100) SP signals. No such problems occur in SP−PLP experiments for monomers of low k_t and high k_p, where a significant fraction of the monomer is polymerized by applying a single laser pulse, and the resulting conversion vs time traces thus are of excellent signal-to-noise quality. With dodecyl acrylate, for example, a single laser pulse may induce a monomer conversion of several percent.[1,10]

Bulk homopolymerization k_t data from PLP methods have become available for several acrylates (methyl acrylate (MA),[10,11] butyl acrylate (BA),[12] and dodecyl acrylate (DA)[10]) and for methacrylates (methyl methacrylate (MMA),[9] butyl methacrylate (BMA),[13] and dodecyl methacrylate (DMA)[13,14]). It appeared worthwhile to extend such k_t studies to bulk copolymerizations. The interest in these investigations is 2-fold: (i) Copolymerization k_t should be very helpful to improve the understanding of mechanisms controlling (radical−radical) termination processes. (ii) Free-radical copolymerizations are of enormous technical importance, and strategies to model termination behavior of systems containing more than one monomer are urgently needed. Only a very few investigations into copolymerization k_t are found in the literature. Russo and Munari studied the styrene−MMA and styrene−BA systems.[15] k_t in MMA−BMA and MMA−DMA copolymerizations has been investigated by Ito and O'Driscoll.[16] These data and results for several less common monomer systems are contained in the excellent survey on free-radical copolymerization kinetics by Fukuda et al.[17] This article

10.1021/ma9814806 CCC: $18.00

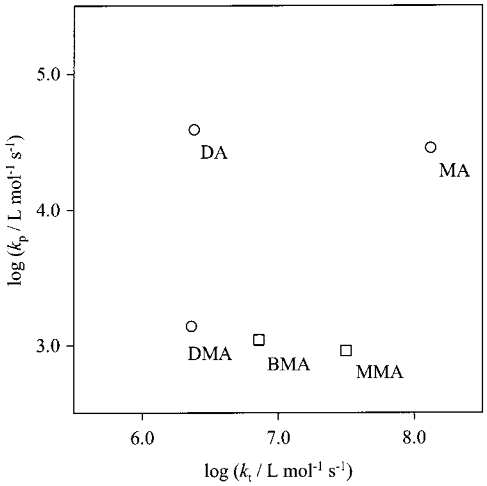

Figure 1. Propagation rate coefficients, k_p, and termination rate coefficients, k_t, for several acrylates and methacrylates at 40 °C and 1000 bar. The circles indicate the monomers under investigation in this work (DA, MA, and DMA). The data are from refs 9, 10, 23, and 24.

also summarizes the existing knowledge on modeling of copolymerization k_t.

The present paper aims at providing the first investigation into termination kinetics in bulk free-radical copolymerization that is exclusively based on data from pulsed-laser techniques. The systems DA–DMA and DA–MA were selected for this study. The arguments for choosing these particular systems will be outlined by means of Figure 1, where the termination and propagation rate coefficients of MA, DA, MMA, BMA, and DMA homopolymerizations are given for 40 °C and 1000 bar on a double-log scale. High-pressure k_p and k_t data are plotted as most of our experiments have been carried out under such conditions. Toward higher pressure the propagation rate is enhanced and termination rate is diminished, which results in a significant improvement of signal-to-noise quality of the SP–PLP experiments. It should, however, be noted that no qualitative difference would be seen if the kinetic data in Figure 1 were plotted for ambient conditions, e.g., for 1 bar and 30 °C. Another point that needs to be made before commenting on the k_p and k_t data in Figure 1 relates to range of monomer conversion where these numbers apply: Whereas k_p does not depend on conversion, unless very high degrees of monomer conversion are reached, k_t may significantly vary with conversion (and also with free-radical chain length and with the type of polymer that is produced, e.g., low or high molecular weight material). The k_t data in Figure 1 refer to the initial plateau region where, in most (meth)acrylate homopolymerizations, the termination rate coefficient remains constant. As will be shown below, this range extends up to a monomer conversion of about 15% in MA homopolymerization, but at least up to 40% in DA and DMA homopolymerizations. An exception to such an initial conversion-independent k_t behavior seems to occur with BA where a slight enhancement in k_t is seen up to 10% conversion.[12] It is for this reason that BA is not included in Figure 1. Further studies into BA termination behavior are underway.

In Figure 1, a family type behavior of k_p is seen for the methacrylates and for the acrylates (BA[12] fits into this pattern with k_p being between the k_p's of DA and MA). No such family type behavior is observed for the termination rate coefficient: k_t of methyl acrylate is by almost 2 orders of magnitude above k_t of DA. A significant increase in k_t in going from the dodecyl to the methyl member is also seen within the methacrylate family. It appears to be a matter of priority to understand why k_t is so different within monomer families (of almost identical k_p). Copolymerization studies should provide valuable insights with measurements on the DA–MA system being of particular interest: The homopolymerization k_p's of MA and DA differ only by a factor of 1.4 whereas the k_t's are significantly apart, by a factor of 55 (with all these numbers referring to 40 °C and 1000 bar). Just the opposite is true for the DA–DMA system: The k_t's are very close to each other whereas the k_p's differ by a factor of 29. Thus, DA–DMA copolymerization was chosen as the second system to be investigated. A further important argument for selecting these two systems, with DA being one of the comonomers, relates to the (above-mentioned) enhanced signal-to-noise quality in SP–PLP experiments with monomers that are low in k_t and high in k_p.

The experimental procedure used within the present study is as follows: Copolymerization k_p/k_t values are derived from SP–PLP experiments. This $(k_p/k_t)_{copo}$ data in conjunction with $k_{p,copo}$ from separate copolymerization PLP–SEC experiments yields $k_{t,copo}$. The entire set of experiments has been carried out at 40 °C and 1000 bar.

Experimental Section

This part will be kept very brief as descriptions of the SP–PLP setup have been given elsewhere.[6,9] The principal components of the SP–PLP setup are a Lextra 50 excimer laser (Lambda Physics) of 20 ns pulse width which is operated on the XeF line at 351 nm, a 75 W tungsten halogen lamp (General Electric) powered by two batteries (12 V, 180 A/h), a BM 50 monochromator (B&M Spectronic), and a fast near-infrared (NIR) InAs detector (EG & G, Judson) of 2 μs time resolution. Monomer conversion is measured via the NIR absorbance of C–H modes (at the C=C double bond) around 6200 cm^{-1}. The detector signal is recorded on a 12 bit transient recorder (ADAM TC 210-1, Rene Maurer) and transferred to an IBM-compatible personal computer.

PLP–SEC experiments (to measure copolymerization k_p) have only been performed for the DA–DMA system at a laser pulse repetition rate of 100 Hz. SEC analyses were carried out by Dr. I. Lacik (Polymer Institute of Slovak Academy of Sciences, Bratislava) on a Waters instrument at 30 °C with PSS SDV columns using tetrahydrofuran as the eluent. The Mark–Houwink coefficients that are needed to derive copolymer molecular weights were determined by Polymer Standards Service (Mainz, Germany). These copolymer PLP–SEC investigations will be detailed within a separate paper on $k_{p,copo}$ of several acrylate–acrylate, acrylate–methacrylate, and methacrylate–methacrylate systems.[18]

DA (Fluka), which is actually a mixture of dodecyl acrylate (55%) and tetradecyl acrylate (45%), MA (Fluka, 99%), and DMA (Fluka, 99%) were distilled under reduced pressure in the presence of K_2CO_3 to remove the inhibitor hydroquinone monomethyl ether. Oxygen was removed by several freeze–pump–thaw cycles. In a glovebox under an argon atmosphere, the comonomer mixtures are prepared, DMPA (2,2-dimethoxy-2-phenylacetophenone (Aldrich, 99%) is added to yield a photoinitiator concentration of about 5 × 10^{-3} mol L^{-1}, and the reaction mixture is filled into an internal cell.[19] This internal cell (consisting of a Teflon tube into which two CaF_2 windows are fitted) is inserted into the high-pressure cell[19] and irradiated with 351 nm excimer laser light at individual pulse energies of 2–3 mJ.

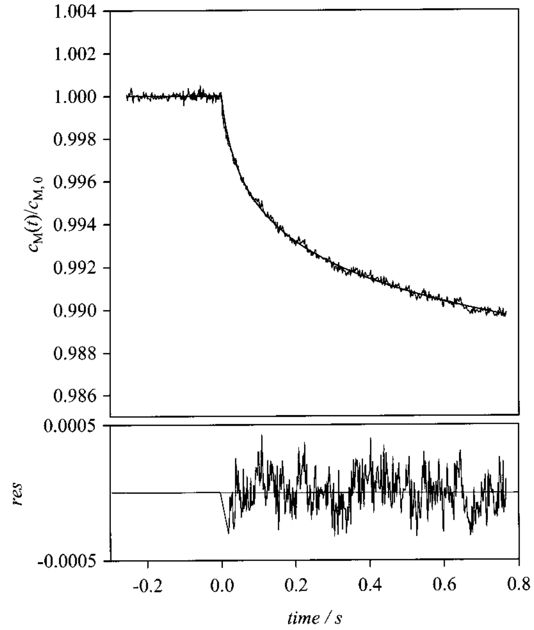

Figure 2. Monomer concentration vs time trace of a methyl acrylate–dodecyl acrylate copolymerization at equimolar amounts of both monomers measured for a reaction mixture at 40 °C, 1000 bar, and 5 wt % initial ($t = 0$) copolymer concentration. The signal is obtained by co-adding three single laser pulses. The difference between measured and fitted (eq 1) data is illustrated by plotting the residuals (res) in the lower part of Figure 2.

Monomer conversion induced by a single laser pulse is recorded via time-resolved online NIR spectroscopy at 6170 ± 15 cm^{-1}. The band maximum positions of the three monomers occur close to each other: 6165 cm^{-1} (DA), 6171 cm^{-1} (MA), and 6166 cm^{-1} (DMA) with these wavenumbers referring to 40 °C and 1000 bar. A single absorption band is obtained for both pure monomers and monomer mixtures. To measure total monomer conversion, the high-pressure cell is repeatedly inserted into the sample compartment of a Fourier transform IR/NIR spectrometer (Bruker IFS-88), and absorbance spectra are recorded in the 6100–6250 cm^{-1} range. As the integrated molar absorptivities of the three monomers are rather similar in this spectral range and as no significant drift in monomer composition occurs in the conversion range of the present study, monomer concentrations may be derived from the integrated absorbance of this characteristic band.[8] The drift with conversion of the comonomer mixture concentration is easily estimated from reactivity ratio data that have been determined for both systems under reaction conditions via ^{1}H NMR analysis carried out on copolymeric products obtained at low conversion.[18]

Results

The entire set of experimental data refers to 40 °C and 1000 bar. In Figure 2, for the copolymerization of an equimolar mixture of DA and MA the spectroscopically measured change in relative monomer concentration, $c_M(t)/c_{M,0}$, is plotted as a function of time t (after applying the laser pulse at $t = 0$). The copolymer concentration at $t = 0$, resulting from monomer conversion by previous pulsing, was 5 wt % in that particular experiment. $c_{M,0}$ is the overall (DA plus MA) monomer concentration at $t = 0$. The relative change in overall monomer conversion induced by a single laser pulse in this particular experiment is 1% after about 600 ms. Fitting of the measured $c_M(t)/c_{M,0}$ vs t data to eq 1 yields k_p/k_t (or k_t/k_p) and also $k_tc_{R,0}$, where $c_{R,0}$ refers to the free-radical concentration that is instantaneously produced by laser-induced decomposition of (part of) the photoinitiator.

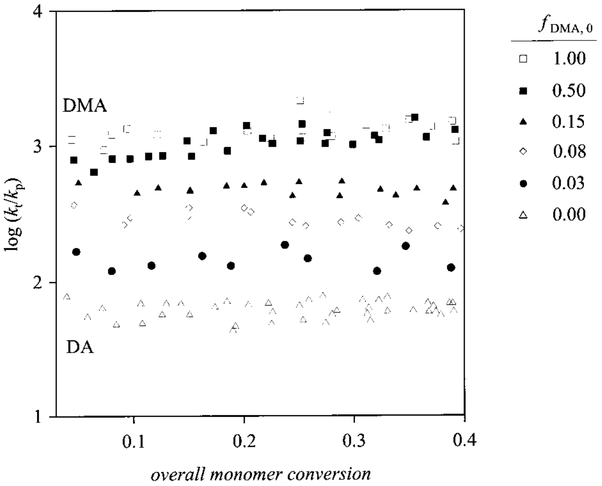

Figure 3. k_t/k_p of DA–DMA bulk copolymerizations at 40 °C and 1000 bar plotted against overall monomer conversion. $f_{DMA,0}$ = mole fraction of DMA in the (initial) comonomer mixture.

$$\frac{c_M(t)}{c_{M,0}} = (2k_tc_{R,0}\,t + 1)^{-k_p/2k_t} \qquad (1)$$

k_t in eq 1 refers to the termination rate law in eq 2:

$$\frac{dc_R}{dt} = -2k_tc_R^{\,2} \qquad (2)$$

In eqs 1 and 2, k_t is considered to be independent of free-radical chain length. Actually, termination in SP–PLP experiments primarily occurs by reaction of two radicals that are very similar in size. In principle, a termination rate coefficient $k_t(i,i)$, with chain length i increasing linearly with time t, should be used to model SP–PLP experiments (at least under conditions where chain-transfer processes are not important). On the other hand, as can be seen from the plot of residuals (res) in the lower part of Figure 2, it turns out that a chain-length-independent k_t value allows for an adequate representation of the measured $c_M(t)/c_{M,0}$ vs t trace. Also, for each of the other homo- and copolymerization SP–PLP experiments of the present study a very satisfactory fit of measured $c_M(t)/c_{M,0}$ vs t data to eq 1 is obtained over extended ranges of t in which free-radical chain length continuously and significantly increases. Within the remainder of this paper, a chain-length-independent (average) k_t is assumed to reasonably represent termination kinetics. Equation 1 is thus used to derive a value of k_t/k_p from each SP–PLP experiment.

During the course of DA–DMA and DA–MA bulk copolymerizations at different initial monomer concentrations, several such individual SP–PLP have been carried out. Figure 3 shows the resulting k_t/k_p data for the DA–DMA system, as obtained by fitting to eq 1 the $c_M(t)/c_{M,0}$ vs t traces from experiments at initial DMA mole fractions, $f_{DMA,0}$, of 0.03, 0.08, 0.15, and 0.50. It is easily deduced from the measured reactivity ratios,[18] $r_{DA} = 0.93$ and $r_{DMA} = 2.81$, that the monomer mixture composition stays very close to the initial composition, $f_{DMA,0}$, at conversions up to 0.4 (40% overall monomer

Table 1. Copolymerization Rate Coefficient Data $(k_t/k_p)_{copo}$, $k_{p,copo}$, and $k_{t,copo}$ for the Systems DA–MA and DA–DMA Studied by SP–PLP Experiments

system	$f_{MA(DMA),0}$	$\log(k_t/k_p)_{copo}$	$\log(k_{p,copo}/$ L mol^{-1} s$^{-1})^a$	$\log(k_{t,copo}/$ L mol^{-1} s$^{-1})$
DA/MA	0.00	1.78	4.60	6.38
	0.25	2.25	4.55	6.80
	0.50	2.65	4.52	7.17
	0.80	3.28	4.48	7.76
	1.00	3.67	4.46	8.13
DA/DMA	0.00	1.78	4.60	6.38
	0.03	2.13	4.27	6.40
	0.08	2.43	3.99	6.42
	0.15	2.63	3.80	6.43
	0.50	2.99	3.45	6.44
	1.00	3.10	3.27	6.37

[a] The $k_{p,copo}$ data are from PLP–SEC experiments for DA–DMA and are estimated via the IPUE model for DA–MA (see text).

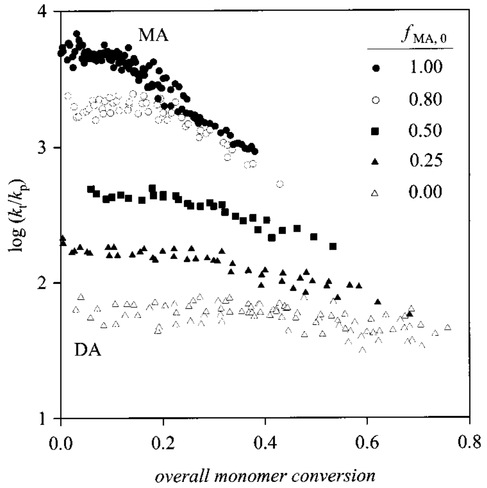

Figure 4. k_t/k_p of DA–MA bulk copolymerizations at 40 °C and 1000 bar plotted against overall monomer conversion. $f_{MA,0}$ = mole fraction of MA in the (initial) comonomer mixture.

conversion). The k_t/k_p values measured for the homopolymerizations of DA[10] and DMA[13] are also given in Figure 3. No significant variation of k_t/k_p with the degree of (overall) monomer conversion is seen for either the homo- or copolymerizations. Thus, arithmetic mean values of log k_t/k_p taken over the entire conversion range up to 40% have been derived for each composition, $f_{DMA,0}$, including the situations of $f_{DMA,0} = 0$ and $f_{DMA,0} = 1$. These data are summarized in the second column of Table 1. Another interesting point to note from Figure 3 is that k_t/k_p stays independent of the composition of the monomer mixture between $f_{DMA,0} = 1.0$ and $f_{DMA,0} = 0.5$ but strongly varies toward lower DMA contents, in particular at DA mole fractions above 0.92 ($f_{DMA,0}$ below 0.08).

The log k_t/k_p vs (overall) monomer conversion data for DA–MA copolymerizations at initial MA contents of $f_{MA,0} = 0.25$, 0.50, and 0.80 are plotted together with the corresponding homopolymerization data for DA[10] and MA[12] in Figure 4. The results for DA at monomer conversions up to 40% are the same as in Figure 3. Even within the enlarged conversion range of Figure 4, up to almost 80% (which is equivalent to a polymer content of 80 wt %), no clear change in k_t/k_p is seen for DA. It should be noted that at such high polymer contents viscosity will exceed the pure monomer viscosity by several orders of magnitude. In MA homopolymerization k_t/k_p clearly depends on conversion. A plateau region of invariant k_t/k_p extends only up to about 15% overall monomer conversion, and a pronounced decrease in k_t/k_p is seen upon further polymerization. The MA reaction could not be followed to conversions above 40% as the system then became inhomogeneous. The significant reduction in k_t/k_p at MA conversions above 15% results from diffusion control of the termination rate coefficient. A corresponding change has also been found for MA homopolymerization at other pressures and temperatures.[10] Order of magnitude changes in k_t as a function of monomer conversion are known to occur in bulk homopolymerizations of methyl methacrylate[20] and styrene.[21] The origin of these enormous changes has been discussed by several groups[22] and is still an active field of research. The present paper will not deal with these effects but focus on the initial plateau region of constant k_t/k_p. Figure 4 shows that this plateau range increases with the DA content of the copolymerizing DA–MA mixture (as does the range where the reaction may be carried out in homogeneous phase and thus kinetic data may be obtained from SP–PLP). Another interesting point to note from Figure 4 is the regular change in log k_t/k_p with $f_{MA,0}$. The arithmetic mean values of log k_t/k_p obtained for the initial plateau region are also given in Table 1.

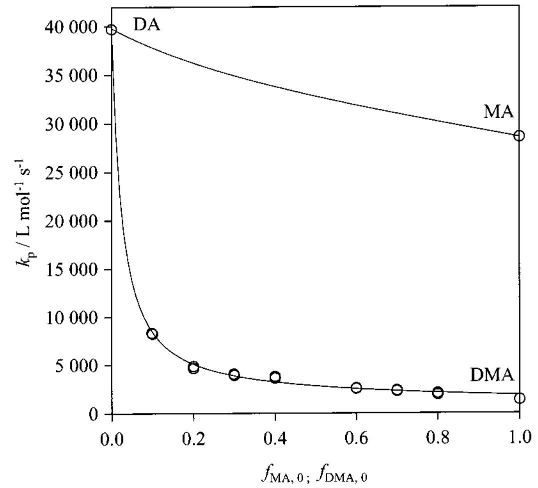

Figure 5. Propagation rate coefficients of DA–MA and DA–DMA copolymerizations at 40 °C and 1000 bar, plotted against the mole fraction of MA and DMA, respectively. The DA–MA data are obtained via the IPUE model (eqs 3a and 3b). The DA–DMA data are measured by PLP–SEC (see text).

It is beyond the scope of this paper to present and discuss the copolymerization k_p data measured for several DA–DMA (at 40 °C and 1000 bar) in any detail. This material will be given elsewhere.[18] The numbers obtained are plotted in Figure 5. The homopolymerization k_p's are from refs 23 and 24. The PLP experiments were carried out with 2,2-dimethoxy-2-phenylacetophenone as the photoinitiator at pulse repetition rates of 100 Hz. The copolymer from reaction at (overall) monomer conversions below 7% was subjected to SEC analysis with THF acting as the eluent. A pronounced PLP structure of the molecular weight distribution, with up to three inflection points, is observed. Via the Mark–Houwink coefficients for DA–DMA copolymers,[18] the $k_{p,copo}$ values are obtained from the position of the first of these points of inflection according to the procedure outlined, e.g., in ref 5. The characteristic features of the DA–DMA data in Figure 5, a steep decrease in k_p upon the addition of small amounts of DMA to DA and an extended region with only a slight reduction in k_p at DMA monomer mole fractions above 20%, are very similar to what has been observed for the BA−MMA system by Hutchinson et al.[5] From the line through the DA−DMA data (which actually is a fit according to the explicit penultimate unit effect (EPUE) model)[18] $k_{\mathrm{p,copo}}$ data for the monomer mixture compositions of the SP−PLP experiments were estimated. It is not the purpose of the present paper to address the issue of modeling $k_{\mathrm{p,copo}}$ by EPUE or IPUE models.[25] The EPUE model has been chosen for the simple reason that it provides a better representation of the experimental DA−DMA k_{p} data and is thus well suited to estimate k_{p} values as required for deriving $k_{\mathrm{t,copo}}$ from the $k_{\mathrm{t}}/k_{\mathrm{p}}$ data from single pulse experiments. These numbers are presented in the third column of Table 1. Combining $k_{\mathrm{p,copo}}$ with $(k_{\mathrm{p}}/k_{\mathrm{t}})_{\mathrm{copo}}$ yields the $k_{\mathrm{t,copo}}$ data which are given in the last column of Table 1.

PLP−SEC experiments for the DA−MA system have not yet been carried out. Because of the similarity of the two homopolymerization k_{p}'s, it appeared justified to estimate $k_{\mathrm{p,copo}}$ via the IPUE model. In view of the enormous difference in homopolymerization k_{t}'s, such $k_{\mathrm{p,copo}}$ values should be sufficient to provide a reasonable separation of the k_{p} and k_{t} contributions to $(k_{\mathrm{p}}/k_{\mathrm{t}})_{\mathrm{copo}}$. The simplified IPUE procedure assumes the two radical reactivity ratios, s_{DA} and s_{MA}, to be identical and to be given by the square root of the product of the reactivity ratios, r_{DA} and r_{MA}. These two reactivity ratios were determined by ^{1}H NMR analysis of DA−MA copolymer samples prepared at 40 °C and 1000 bar to be $r_{\mathrm{DA}} = 0.70$ and $r_{\mathrm{MA}} = 0.78$. According to the simplified IPUE model, this results in the radical reactivity ratios $s_{\mathrm{DA}} = s_{\mathrm{MA}} = 0.74$. From these numbers and from the homopolymerization k_{p} values of DA[23] and of MA,[23] copolymerization k_{p} is calculated via the IPUE relations (eqs 3a and 3b):

$$k_{\mathrm{p,copo}} = \frac{r_1 f_1^{\,2} + 2 f_1 f_2 + r_2 f_2^{\,2}}{\dfrac{r_1 f_1}{k_{\mathrm{p}11}} + \dfrac{r_2 f_2}{k_{\mathrm{p}22}}} \tag{3a}$$

r_i denotes the reactivity ratios, and f_i is the mole fraction of monomer i in the reaction mixture. $k_{\mathrm{p}ii}$ is given by eq 3b

$$k_{\mathrm{p}ii} = \frac{r_i f_i + f_j}{r_i f_i + f_j/s_i} \tag{3b}$$

The line plotted for DA−MA in Figure 5 is calculated from eqs 3a and 3b. The $k_{\mathrm{p,copo}}$ values estimated for the conditions of the SP−PLP copolymerization experiments are listed in Table 1 as are the values for $k_{\mathrm{t,copo}}$ resulting from $k_{\mathrm{p,copo}}$ and $(k_{\mathrm{p}}/k_{\mathrm{t}})_{\mathrm{copo}}$.

Discussion

The $k_{\mathrm{t,copo}}$ values for 40 °C and 1000 bar of the two copolymerization systems, DA−DMA and DA−MA, are plotted together with the corresponding homopolymerization values in Figure 6.

On the log $k_{\mathrm{t,copo}}$ vs mole fraction ($f_{\mathrm{MA,0}}$ or $f_{\mathrm{DMA,0}}$) scale, the data for each system closely fit to a straight line between the associated homotermination rate coefficients. It should be noted that the $k_{\mathrm{t,copo}}$ data are derived from two completely independent experiments, SP−PLP and PLP−SEC. The $k_{\mathrm{t,copo}}$ values for DA−DMA demonstrate that the very pronounced variation of $(k_{\mathrm{p}}/k_{\mathrm{t}})_{\mathrm{copo}}$ with $f_{\mathrm{DMA,0}}$ at low DMA contents (Figure 3) reflects the associated variation in $k_{\mathrm{p,copo}}$ (Figure 5). For the special situation of the two homotermination rate coefficients, $k_{\mathrm{t,DA}}$ and $k_{\mathrm{t,DMA}}$, being almost identical, $k_{\mathrm{t,copo}}$ is close to these values and independent of the monomer mixture composition. This result is perhaps not overly surprising as one might expect that $k_{\mathrm{t,copo}}$ behaves like this in cases where the two homopolymerization k_{t}'s are the same.

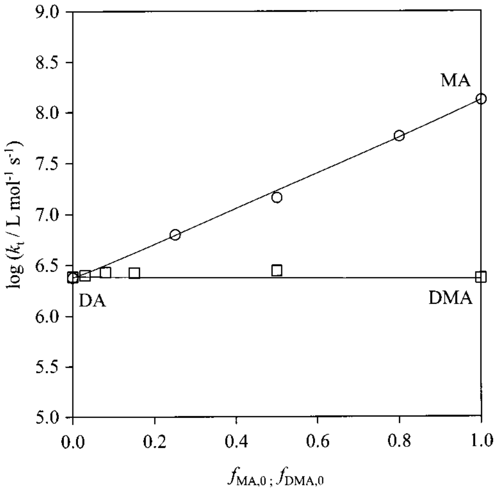

Figure 6. Termination rate coefficients (in the plateau region, see text) of dodecyl acrylate (DA)−methyl acrylate (MA) and dodecyl acrylate (DA)−dodecyl methacrylate (DMA) copolymerizations at 40 °C and 1000 bar, plotted against the (initial) mole fraction of MA and DMA, respectively. The procedure of deriving $k_{\mathrm{t,copo}}$ is outlined in the text. The lines are obtained by fits according to model D.

That an approximately linear log $k_{\mathrm{t,copo}}$ vs $f_{\mathrm{MA,0}}$ relation is also found for the DA−MA system where the homopolymerization k_{t}'s differ by almost 2 orders of magnitude could not be expected. Whereas several models should be capable of describing the situation met with DA−DMA, it is very challenging to try to model and understand the $k_{\mathrm{t,copo}}$ behavior in DA−MA copolymerization.

Modeling of $k_{\mathrm{t,copo}}$ has been thoroughly addressed by Fukuda et al.[17] We considered four of the models presented in ref 17 to fit our $k_{\mathrm{t,copo}}$ data for DA−DMA and DA−MA.

Model A, which has been proposed by Fukuda, assumes diffusion-controlled termination to be related to the composition of the produced copolymer according to eq 4:

$$\text{model A:} \qquad k_{\mathrm{t,copo}}^{\ \ -1} = k_{\mathrm{t}11}^{\ \ -1} F_1 + k_{\mathrm{t}22}^{\ \ -1} F_2 \tag{4}$$

where F_i is the mole fraction of comomoner i segments within the copolymer.

In *model B*, two types of free radicals, one with a monomeric unit 1 and the other with a monomer 2 unit at the chain end, are considered to sufficiently account for copolymerization k_{t} according to

$$\text{model B:} \quad k_{\mathrm{t,copo}} = k_{\mathrm{t}11} P_1^{\,2} + 2 k_{\mathrm{t}12} P_1 P_2 + k_{\mathrm{t}22} P_2^{\,2} \tag{5a}$$

where the $k_{\mathrm{t}ii}$'s are the homotermination rate coefficients and the P_i's are the relative populations of the two types of "terminal" free radicals ($P_1 = 1 - P_2$). Φ, which is referred to as the Walling factor,[26] describes the size of the cross-termination rate coefficient ($k_{\mathrm{t}12} = k_{\mathrm{t}21}$) relative to the geometric mean of the homopolymerization rate coefficients:

$$\Phi = \frac{k_{t12}}{(k_{t11}k_{t22})^{0.5}} \tag{5b}$$

It should be noted that a so-called geometric mean rule, which is formally identical to eq 5b, has been frequently used in free-radical gas kinetics to estimate cross-recombination rate coefficients k_{AB} from the associated homorecombination rate coefficients k_{AA} and k_{AB}.[27]

Two other models given in Fukuda et al.'s article,[17] C and D, in addition to the terminal unit also consider the penultimate unit at the free-radical chain end as has first been tried by Russo and Munari.[15] These models are associated with an enhanced number of termination rate coefficients. Given in eq 6 is the expression for $k_{t,copo}$ of a binary copolymerization, for which 10 termination rate coefficients, $k_{tij,kl}$, need to be considered. $k_{tij,kl}$ refers to the reaction of (two) radicals terminating in the monomer units ij and kl, respectively. The P_{ij}'s and P_{kl}'s indicate relative populations of the four types of "penultimate" free radicals (with chains ending in units 11, 12, 21, and 22, respectively). These populations are available from the propagation rate coefficients and reactivity ratios.[25]

$$k_{t,copo} = \sum_{l=1}^{2}\sum_{k=1}^{2}\sum_{i=1}^{2}\sum_{j=1}^{2} P_{ij}P_{kl}k_{tij,kl} \tag{6}$$

To reduce the relatively large number of termination rate coefficients, *model C* replaces rate coefficients for reaction between "unlike" free radicals, $k_{tij,kl}$ (with ij being different from kl), by the corresponding coefficients for termination of the "like" radicals, $k_{tij,ij}$ and $k_{tkl,kl}$, via the arithmetic mean approximation in eq 7:[17]

$$k_{tij,kl} = 0.5(k_{tij,ij} + k_{tkl,kl}) \tag{7}$$

Using eq 7 to eliminate all "unlike" termination rate coefficients turns eq 6 into eq 8, which contains only the four "like" (penultimate) termination coefficients:

$$\text{model C:}\quad k_{t,copo} = k_{t11,11}P_{11} + k_{t21,21}P_{21} + k_{t22,22}P_{22} + k_{t12,12}P_{12} \tag{8}$$

Model D differs from model C in that a geometric mean approximation (eq 9) is applied to reduce the number of penultimate termination rate coefficients from 10 to four:

$$k_{tij,kl} = (k_{tij,ij}k_{tkl,kl})^{0.5} \tag{9}$$

Equation 9 is the expression used by Fukuda et al.[17] Russo and Munari in their pioneering study had an additional factor of 2 on the right-hand side of eq 9 with this formulation being identical to what is used in gas kinetics to estimate cross-termination.[27]

Substituting eq 9 into eq 6 yields the expression (eq 10) for $k_{t,copo}$ according to *model D*:

$$\text{model D:}\quad {k_{t,copo}}^{0.5} = {k_{t11,11}}^{0.5}P_{11} + {k_{t21,21}}^{0.5}P_{21} + {k_{t22,22}}^{0.5}P_{22} + {k_{t12,12}}^{0.5}P_{12} \tag{10}$$

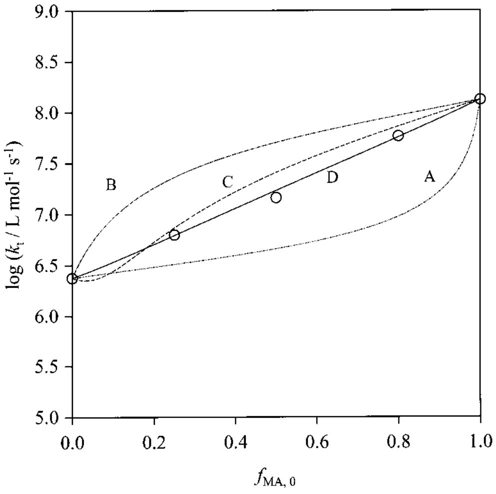

Figure 7. Termination rate coefficients (in the plateau region, see text) of MA–DA copolymerization at 40 °C and 1000 bar, plotted against the mole fraction of MA. The lines (A) through (D) correspond to the copolymerization k_t models given in the text.

Fukuda et al.[17] presented model D in a slightly different way (eq 11) with the two penultimate rate coefficients, $k_{t12,12}$ and $k_{t21,21}$, being replaced by two parameters δ_1 and δ_2:

$$\text{model D}'\text{:}\quad {k_{t,copo}}^{0.5} = {k_{t11,11}}^{0.5}(P_{11} + \delta_1 P_{21}) + {k_{t22,22}}^{0.5}(P_{22} + \delta_2 P_{12}) \tag{11}$$

δ_i^2 is defined as

$$\delta_i^{\,2} \equiv \frac{k_{tji,ji}}{k_{tii,ii}}$$

The ability of models A through D to represent the k_t values measured for the DA–MA copolymerization is demonstrated in Figure 7. Models A and B, which both consider only two types of terminating free radicals, seriously fail to represent the experimental $k_{t,copo}$ data. The line referring to model B has been calculated under the assumption that eq 5b holds with $\Phi = 1$. Even major changes in Φ do not result in a significantly improved quality of representing the experimental data by model B. Also, model C, which assumes diffusion control with four kinds of penultimate free radical species, fails to provide an adequate fit of the measured $k_{t,copo}$ data. Model D, on the other hand, allows for an excellent representation of the experimental data. It should be noted that the line through the DA–DMA data in Figure 6 is not obtained just from a linear least-squares procedure but is derived from a fit to model D. The almost linear change of log $k_{t,copo}$ with monomer feed composition f should be particularly noted. This result certainly bears important mechanistic information. Moreover, this linear correlation may be useful for predicting or estimating copolymerization k_t.

The copolymerization rate coefficients for termination between the two types of "like" penultimate radicals, $k_{t12,12}$ and $k_{t21,21}$, as obtained from fitting the $k_{t,copo}$ data for DA–MA and for DA–DMA to model D, are listed in Table 2. As is to be expected, these coefficients are identical and are close to the associated homopolymerization values, $k_{t11,11}$ and $k_{t22,22}$, for the DA–DMA system. Also, for the DA–MA system, the $k_{t12,12}$ and $k_{t21,21}$ coefficients are very close to each other. These coefficients are clearly different from the homotermination values but are between $k_{t11,11}$ and $k_{t22,22}$.

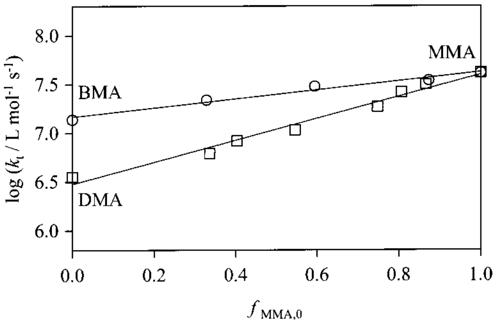

Figure 8. Termination rate coefficients from Ito and O'Driscoll[16] for dodecyl methacrylate (DMA)−methyl methacrylate (MMA) and butyl methacrylate (BMA)−methyl methacrylate (MMA) copolymerizations at 30 °C and ambient pressure. The data in ref 16 are given as relative rate coefficients $k_{t,copo}/k_{t,homo}$. The $k_{t,copo}$ values were calculated using $k_{t,homo}$ from ref 9. The lines are obtained by linearly fitting the data.

The close-to-linear correlation that is seen for both the DA−DMA and DA−MA system asks for presenting the literature data of similar systems also as log $k_{t,copo}$ vs f plots. For MMA−BMA and MMA−DMA copolymerizations at 30 °C and ambient pressure, Ito and O'Driscoll[16] reported $k_{t,copo}$ data that were deduced from rotating sector experiments. They plotted $k_{t,copo}$ vs the monomer feed composition and obtained curved dependences. The very remarkable observation from Figure 8 is that this literature data also closely fit to a linear log $k_{t,copo}$ vs f behavior. Ongoing studies[28] into other (meth)acrylate copolymerization systems, e.g., DA−BA and BA−MMA, also yield approximately linear plots of log $k_{t,copo}$ vs f. Model D thus turns out to be well suited for representation of these systems. Further examples for the suitability of model D are given in ref 17.

The data in Figures 6 and 8 suggest that $k_{t,copo}$ might be generally accessible from homotermination data. This, however, is not true. The linear log $k_{t,copo}$ vs f correlation will certainly be restricted to situations where the same mechanism controls termination behavior. This can be seen from Figure 4. Under conditions where homo-k_t of MA varies with monomer conversion (which indicates a change in the mode of termination rate control), the linear log $k_{t,copo}$ vs f correlation is no longer valid. At total momomer conversions between 20% and 35%, the log(k_t/k_p) values for $f_{MA,0} = 1.00$ and 0.80 are almost the same, and linear plots as in Figures 6 and 8 can no longer be drawn at this stage of the reaction. Another argument against any oversimplification of $k_{t,copo}$ behavior is seen in the Fukuda et al. paper[17] where copolymer systems with a pronounced curvature on the log $k_{t,copo}$ vs f plots are presented. Also, in these systems, the mechanism that controls k_t may be quite different for the two (copolymerizing) monomers. It should be noted, however, that even under conditions where no linear log $k_{t,copo}$ vs f correlation is obtained, model D is capable of adequately representing the copolymerization k_t behavior.

The results for $k_{t,copo}$ may be summarized as follows: Model D allows for a very satisfactory fitting of the experimental material that is presently available. In cases where the mode of diffusion control (probably) is the same, as in the initial plateau region of (meth)acrylate copolymerizations, the dependence of $k_{t,copo}$ on monomer feed composition appears to be particularly simple, and an (almost) linear log $k_{t,copo}$ vs f correlation is seen. In these (meth)acrylate copolymerizations, model D may perhaps be further simplified: The data in Table 2 indicate that $k_{t12,12}$ and $k_{t21,21}$ are very close to each other, which also seems to be the case for the other (meth)acrylate copolymerization systems. This would allow to reduce the number of parameters required for $k_{t,copo}$ modeling from two to one.

Table 2. Termination Rate Coefficients for the Reaction of "Like" Radicals As Deduced from Model D for the DA−MA and DA−DMA Copolymerization Systems

system	log($k_{t\ 12,12}$/L mol^{-1} s^{-1})	log($k_{t\ 21,21}$/L mol^{-1} s^{-1})
DA/MA	6.79	6.71
DA/DMA	6.37	6.37

The excellent representation of $k_{t,copo}$ via model D must not necessarily mean that the underlying concept of termination control by a penultimate unit effect is truly operative. Also other mechanisms may result in expressions that are mathematically close to, or even identical to, eq 10 (or to an even further simplified version of this equation, with the second and the fourth term on the right-hand side of eq 10 being joined together, which seems to work for the (meth)acrylate systems). Nevertheless, it appears worthwhile to briefly consider why a penultimate unit effect (PUE) model might be so appropriate to describe termination kinetics. The major argument that we see in favor of such a k_t PUE model considers steric factors, in particular a shielding of the free-radical chain end. Substituents on the terminal and on the penultimate unit should (primarily) contribute to this effect. Steric shielding would also explain the trends in homotermination of (meth)acrylates in the initial plateau region (Figure 1). k_t is expected to strongly increase in going from the dodecyl to the methyl members in the (meth)acrylate families. Moreover, the dominant shielding effect which must be expected to occur with the dodecyl monomers should result in only minor differences in k_t for DA and DMA whereas, under the poor shielding conditions of the methyl members, a significant difference should be seen between the k_t's of MA and MMA resulting from the additional methyl group. This is indeed what is observed. That the differences in homo-k_t's are probably not, at least not exclusively, determined by translational diffusion of macroradicals is indicated by the plateau behavior of k_t in the initial conversion range where viscosity and thus diffusion processes should be strongly affected. Steric arguments provide a reasonable explanation of these characteristic k_t values that are seen in the initial period of several free-radical polymerizations. They also explain why no such plateau value is seen, e.g., in ethene homopolymerization where steric shielding will not be important. Another indication of steric control under the copolymerization conditions of the present work comes from the obvious success of the geometric mean approximation in replacing termination rate coefficients of radicals with "unlike" penultimate units by the corresponding "like" coefficients (eq 9). That steric effects may significantly contribute to k_t is also to be expected from the very low values that have been reported for highly substituted monomers such as itaconates[29] and fumarates.[30]

It goes without saying that, toward higher degrees of monomer conversion where translational diffusion or reactive diffusion[31] become termination rate controlling, the influence of steric arguments will be reduced or will even be lost. It should finally be noted that the plateau region of initial k_t vs monomer conversion behavior has also been assigned to diffusion control by segmental mobility. Actually, Russo and Munari,[15] who introduced the penultimate k_t concept, suggested that rotational motion of a very few units at the chain end determine free-radical diffusion rate via its conformational behavior rather than do motions of larger segments. A clear separation of segmental and steric influences on k_t is certainly difficult. It appears, however, that the remarkable success of the PUE k_t model to fit the copolymerization data is somewhat easier understood in terms of steric hindrance than of segmental mobility. Investigations into further copolymerization systems are required to solve these mechanistic issues, as are studies into the pressure and temperature dependence of copolymerization k_t. Part of this work is already underway in our laboratory.

From the reaction engineering point of view the (almost) linear log $k_{t,copo}$ vs f correlations that have been found within the present study on (meth)acrylates are highly important. They are very useful for estimating termination rate coefficients in binary copolymerizations of (meth)acrylate monomers over fairly extended (initial) conversion ranges. The applicability of model D to fit $k_{t,copo}$ is particularly noteworthy, and further studies will be directed toward elucidating the range of monomers and of polymerization conditions where this model is applicable.

Acknowledgment. The authors are grateful to the Deutsche Forschungsgemeinschaft for supporting this work within the Graduiertenkolleg "Kinetik und Selektivität chemischer Prozesse in verdichteter fluider Phase". Additional support of this work by the Fonds der Chemischen Industrie is gratefully acknowledged. The authors want to thank Professor T. Fukuda for providing additional information on the equations presented in ref 17 and for helpful comments.

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MA9814806