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Termination Kinetics of Methyl Methacrylate Free-Radical Polymerization Studied by Time-Resolved Pulsed Laser Experiments

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ABSTRACT: The SP−PLP technique has been applied to measure k_t/k_p, the ratio of termination to propagation rate coefficients, for the free-radical bulk polymerization of methyl methacrylate at 1000 bar and several temperatures ranging from 40 to 100 °C. k_t/k_p is obtained from time resolved (μs) near-infrared measurement of monomer conversion induced by a single laser pulse of about 20 ns width. A total of 80 such single pulse (SP) signals were co-added to yield a concentration vs time trace of sufficient signal-to-noise quality to deduce k_t/k_p with an accuracy of better than ±40%. With k_p being known from the well-established PLP−SEC procedure, k_t/k_p data directly yield individual (chain-length averaged) termination rate coefficients, referring to a fairly narrow range of monomer conversion. The SP−PLP technique, which seemed to be restricted to investigations into high k_p monomers such as ethene (at high temperatures) and the acrylates, within the present work on MMA is demonstrated to be suitable for kinetic studies on slowly propagating monomers, too.

Introduction

Pulsed-laser techniques have enormously improved the quality of rate coefficient measurements for free-radical polymerization. Applying an excimer laser pulse to a monomer/initiator system almost instantaneously yields a primary concentration, c_R^0, of photoinitiator-derived free radicals. Pulsed-laser polymerization (PLP), with the sample being irradiated by a sequence of evenly spaced laser pulses, in conjunction with analysis of the molecular weight distribution (MWD) of the resulting polymer, preferably by size-exclusion chromatography (SEC), turned out to be a powerful method for the direct measurement of the propagation rate coefficient, k_p. This PLP−SEC method, which traces back to work by Olaj and his group,[1] now constitutes the IUPAC recommended procedure for k_p determination.[2,3] It has been extensively used over the past 10 years to derive accurate k_p values for styrene,[2,4] vinyl esters,[5] acrylates,[6−9] methacrylates,[10−13] and several other monomers[14−16] as a function of temperature and partly up to high pressure.[4,6,10,13]

Studies into termination rate coefficients (k_t) are less frequent. k_t is diffusion-controlled and thus in addition to depending on temperature (T) and pressure (p), as does the chemically controlled coefficient k_p, k_t may be influenced by transport properties that vary with monomer conversion, polymer molecular weight (distribution), polymer architecture, free-radical chain-length, solvent type, and concentration. Applying PLP in conjunction with infrared or near-infrared spectroscopic measurement of monomer conversion induced by a single laser pulse (SP−PLP)[17] or by pulse sequences (PS−PLP)[18,19] allows for the determination of k_t/k_p over wide ranges of T and p and up to higher degrees of monomer conversion. SP−PLP has first been used for studies into ethene kinetics[20] and subsequently to measure free-radical termination of acrylates.[5,21,22] PS−PLP has been applied to measure termination rates of slowly propagating monomers such as styrene[23] and for the methacrylates.[24,25]

The SP−PLP experiment constitutes the by far more powerful and versatile technique as compared to PS−PLP. The monomer conversion induced by a single laser pulse, typically of 20 ns width, is measured by online IR/NIR spectroscopy with a time resolution of microseconds. A chain-length averaged rate coefficient, $\langle k_t\rangle$, is directly obtained from k_t/k_p (with k_p being known from an independent PLP−SEC experiment at identical p and T) for the narrow conversion range of a single experiment, typically extending over no more than 1%. Repeated SP−PLP experiments at several stages during a polymerization to high conversion, allow to determine the dependence of $\langle k_t\rangle$ on monomer conversion. The distribution of free-radical chain lengths after a single pulse is close to a Poisson distribution with chain length i being linearily correlated to time t (after the pulse), unless chain transfer interferes. As a consequence, SP−PLP experiments provide access to investigations into a chain-length dependence of k_t. Actually, termination rate coefficients $k_t(i,i)$ referring to the reaction of two free radicals which are approximately identical in size are found from time-resolved (microsecond) detection of monomer conversion induced by a single laser pulse. As the conversion per pulse is rather small, such an experiment proceeds at (almost) constant polymer concentration, which, at least in principle, allows one to independently map out (monomer) conversion and chain-length dependence of k_t. Unfortunately, the signal-to-noise ratio of monomer conversion vs time traces at present is insufficient to quantitatively detect detailed effects such as a chain-length dependence of k_t.

The PS−PLP experiment is less far-reaching. To derive k_t/k_p from a PS−PLP experiment, where pulse sequences alternating in pulse repetition rate are applied, both rate coefficients, k_p and k_t, need to be constant at least within the conversion range covered by two successive pulse sequences and k_t needs to be independent of chain length. The essential reason PS−PLP (instead of SP−PLP) experiments are carried out is that for several types of monomers the conversion induced by a single pulse is too low to be accurately

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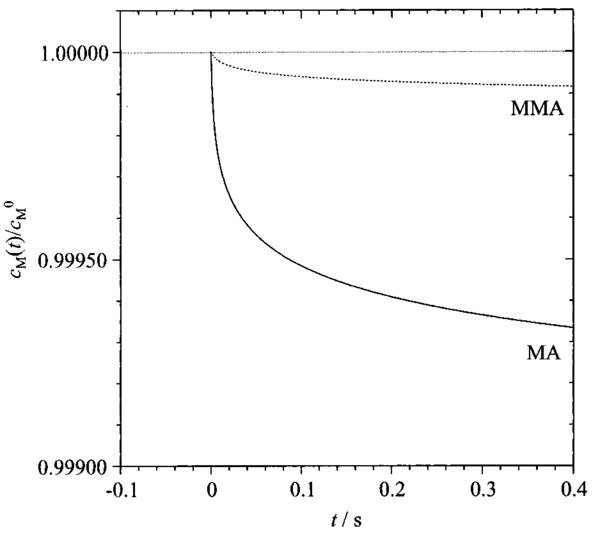

Figure 1. Time-resolved concentration vs time profile calculated from eq 1 for MMA (dotted line) and MA (full line) in SP−PLP experiments at 40 °C, 1000 bar, and 2.5% polymer content. The other parameters that go into the calculation are given in the text.

measured via online spectroscopy. This argument is illustrated in Figure 1, where the time dependence of relative monomer concentration, $c_M(t)/c_M^0$, is plotted vs time t after applying the laser pulse. The data are calculated via eq 1 for SP−PLP experiments in the initial period of methyl acrylate (MA) and methyl methacrylate (MMA) homopolymerizations at 40 °C, 1000, bar and a pulse laser induced primary free-radical concentration c_R^0 of 6 × 10^{-6} mol L^{-1}.

$$\frac{c_M(t)}{c_M^{\ 0}} = (2k_t c_R^{\ 0}\, t + 1)^{-k_p/2k_t} \tag{1}$$

c_M^0 is the monomer concentration prior to applying the single laser pulse, and k_t is the chain-length independent termination rate coefficient. Throughout the subsequent text, experimental k_t values are considered to be chain-length independent (or chain-length averaged) quantities. Moreover, it should be noted that k_t in eq 1 refers to the termination rate law:

$$\frac{dc_R}{dt} = -2k_t c_R^{\ 2} \tag{2}$$

The rate expressions, eqs 1 and 2, rest on the assumption that free-radical decay exclusively proceedes via second-order termination. This assumption may not be valid at very low and very high free-radical concentrations. The applicability of eq 1 for adequate representation of polymerization kinetics may, however, be checked by comparing experimental and fitted (via eq 1) concentration−time profiles over an extended range of t in which free-radical concentration varies significantly.

The rate coefficients, k_p and k_t, that go into the calculation of the conversion-time profiles in Figure 1 are as follows: k_p(MA) = 24 500 L mol^{-1} s^{-1}, k_t(MA) = 1.1 × 10^8 L mol^{-1} s^{-1}, k_p(MMA) = 902 L mol^{-1} s^{-1}, and k_t(MMA) = 2.5 × 10^7 L mol^{-1} s^{-1}. The k_p values for MA and MMA are taken from ref 6 and ref 24, respectively. k_t(MA) is from ref 5. The k_t(MMA) value is estimated from numbers determined by Beuermann[24] for chemically induced bulk polymerizations.

Over the time period up to 0.4 s the MA concentration decays by about 0.07 percent. Kurz succeeded in measuring this small change by microsecond time-resolved near-infrared spectroscopy.[6] Actually a few (up to 10) individual SP−PLP signals were co-added to derive a conversion vs time curve as in Figure 1. For dodecyl acrylate (DA) the conversion induced by one pulse is much larger. A change in monomer concentration by as much as about one percent occurs up to 0.4 s at 1000 bar and 40 °C (not shown in Figure 1), which allows the determination of k_t/k_p from a “true” (i.e., nonaveraged) single pulse experiment. The rate coefficients of DA under these conditions, according to Kurz,[6] are as follows: k_p = 41 300 L mol^{-1} s^{-1} and k_t = 2.47 × 10^6 L mol^{-1} s^{-1}. The degree of monomer conversion induced by one pulse decreases with lower k_p and higher k_t. The concentration change calculated for MMA (Figure 1) is very small. For k_t/k_p determination, a total monomer conversion below 0.01% (after 0.4 s) needs to be detected with a time resolution of microseconds.

Because of the high academic and also technical interest in detailed k_t studies on such slowly propagating monomers too, it appeared worthwhile to try to improve the quality of the SP−PLP procedure and to carry out such experiments on MMA, too. The essential idea was to significantly enhance signal-to-noise by co-adding a larger number of individual SP−PLP signals recorded under virtually the same conditions with only a minor decrease in both MMA and photoinitiator concentration between subsequent “true” single pulse experiments. As the concentration of free radicals originating from the previous pulse decays to a very low level and as small primary radicals are generated by each pulse, the range of chain lengths covered during successively recorded individual concentration vs time traces is identical. The number of co-added signals is limited by the requirement of deriving k_t/k_p for a small range of monomer conversion extending over no more than about 2% to stay close to the intention of “pointwise” probing of the kinetics. In view of the MMA signal depicted in Figure 1, the procedure was modified to allow for co-adding about 100 SP−PLP traces and to deduce k_t/k_p from the resulting monomer conversion vs time curve via a fit by eq 1. The obtained k_t/k_p refers to a conversion range of about 2%. The present paper reports on the first such SP−PLP study on methyl methacrylate. As the conversion per pulse is enhanced for smaller k_t and larger k_p, the experiments have been carried out at high pressures, mostly at 1000 bar.

Experimental Section

The principal components of the SP−PLP setup are a Lextra 50 excimer laser (Lambda Physics) with a pulse width of 20 ns 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 detector unit equipped with a fast InAs detector (EG & G, Judson) with a time resolution of 2 μs.

The irreversible change in intensity of the NIR probing light associated with polymerization induced by each single laser pulse is electronically compensated prior to the arrival of the subsequent pulse. The analogue detector signal is recorded by a 12-bit transient recorder (ADAM TC 210-1, Rene Maurer) and transferred to an IBM-compatible personal computer.

MMA (Fluka), of 99% purity, is distilled under reduced pressure in the presence of dry K_2CO_3 to remove the inhibitor (hydroquinone monomethyl ether) and is treated by several freeze and thaw cycles to remove dissolved oxygen. 2,2-

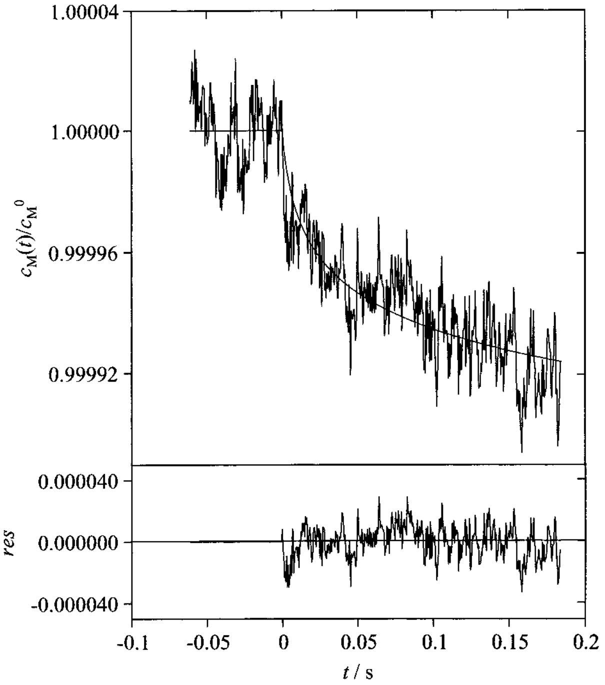

Figure 2. Monomer concentration vs time trace measured during a methyl methacrylate polymerization at 40 °C, 1000 bar, and 9.7% (final) overall MMA conversion. The signal is obtained by co-adding 80 single pulse traces. The difference between measured and fitted (eq 1) data is illustrated by plotting the residuals (*res*) in the lower part of Figure 2.

Dimethoxy-2-phenylacetophenone (Aldrich), which acts as photoinitiator (initial concentration: 5×10^{-3} mol L^{-1}) is added to the monomer and filled into an internal cell[26] under an argon atmosphere. The internal cell is inserted into a high-pressure cell.[26] Irradiation is by excimer laser light (351 nm) at single pulse energies of 2−3 mJ. The resulting monomer conversion is monitored by on-line near-infrared spectroscopy at around 6170 cm^{-1}. Fitting of the time-resolved signal by eq 1 yields k_t/k_p (and $k_t c_R{}^0$ as a second parameter).

After application of a series of single laser pulses, at a repetition rate of 0.2 Hz, with time-resolved measurement of the polymerization induced by each pulse, the optical reaction cell is introduced into the sample chamber of an IFS 88 Fourier transform IR/NIR spectrometer (Bruker) where the absolute (overall) monomer (MMA) concentration is measured. The procedure of deriving MMA concentration from the NIR absorbance in the 6100−6250 cm^{-1} region has been detailed elsewhere.[19] Time-resolved experiments of this kind, each consisting of a series of "true" SP−PLP measurements, are carried out until the polymerizing system becomes inhomogeneous or the photoinitiator is consumed.

Results and Discussion

Plotted in the upper part of Figure 2 is the measured change in relative monomer concentration, $c_M(t)/c_M{}^0$, as a function of time t (after applying the laser pulse) for an MMA bulk polymerization at 40 °C and 1000 bar. The signal results from co-adding the spectroscopically obtained $c_M(t)/c_M{}^0$ data of 80 SP−PLP traces measured within a total of 400 s. During the application of this particular set of 80 single laser pulses, the MMA concentration prior to an individual pulse, $c_M{}^0$, gradually decreases from $0.923 c_M{}^{00}$ to $0.903 c_M{}^{00}$, where $c_M{}^{00}$ refers to the initial pure MMA concentration (or density) at 40 °C and 1000 bar. The kinetic information that is deduced from the kinetic trace in Figure 2 thus refers to overall monomer conversions ranging from 7.7 to 9.7%. For each pulse the MMA concentration is determined with a time resolution of 60 μs via the NIR absorption around 6170 cm^{-1}. The entire signal in Figure 2 consists of 4096 data points. A 25% pre-trigger range (negative t) is recorded for each single pulse signal to ensure that polymerization from the preceding laser pulse has ceased. The curve fitted to the data in Figure 2 is obtained via eq 1. The quality of this fit is illustrated by the plot of residuals in the lower part of Figure 2. No systematic deviation between measured and fitted data can be detected, which provides some evidence for the termination rate law (eq 2) being valid at these experimental conditions. The fit directly yields k_t/k_p and also $k_t c_R{}^0$ (see eq 1). The deduced k_t/k_p values are assumed to be accurate within ±40%.

Table 1. Number of Single Laser Pulses, N_{SP}, Applied in Nine Successive Experiments during an MMA Bulk Polymerization at 40 °C, 1000 bar and the Overall MMA Conversion (Referring to Pure MMA) As Reached after Application of a Particular Series of Laser Pulses (Given in the Last Column)

no.	N_{SP}	overall MMA conversion/%
1	80	1.8
2	80	3.7
3	80	5.7
4	80	7.7
5	80	9.7
6	80	11.6
7	80	13.6
8	80	15.6
9	120	18.5

During each polymerization experiment several such time-resolved measurements have been performed. Table 1 summarizes the number of single pulses, N_{SP}, applied in nine successive experiments during a single MMA bulk polymerization at 40 °C and 1000 bar. Each of these individual experiments yields a relative monomer concentration vs time signal as in Figure 2. The overall monomer conversion, referring to pure MMA, reached after a particular series of single pulses is given in the last column of Table 1. The MMA concentration corresponding to this final conversion after each series of pulses is also the initial concentration, $c_M{}^0$, of the first SP−PLP experiment in the subsequent pulse series of single pulse experiments. The data in Figure 2 are from time-resolved measurement no. 5. The rate coefficients derived from this particular experiment refer to a conversion range of about 2% as do the rate coefficients from the other measurements, with the exception of run no. 9 where 120 single pulses have been applied resulting in a monomer conversion of about 3%, between 15.6 and 18.5%.

From each run (nos. 1−9 in Table 1), k_t/k_p is deduced by fitting the concentration vs time data to eq 1. The resulting values are plotted as open circles in Figure 3 together with data from a second experiment at 40 °C and 1000 bar. Also plotted in Figure 3 are k_t/k_p values obtained during a bulk polymerization at 100 °C and 1000 bar (full circles). Two results immediately emerge from Figure 3: (i) No dependence of k_t/k_p on overall monomer conversion (or polymer content) can be seen at either 40 or 100 °C. This finding is in full agreement with previous studies on MMA.[19,24] (ii) Despite an average scatter in k_t/k_p of ±20% around the mean value given by the horizontal lines, there is no doubt about an increase of k_t/k_p toward lower temperature.

The k_t/k_p data derived as mean values for the initial polymerization range up to about 20% monomer conversion are summarized in Table 2 for MMA bulk poly-

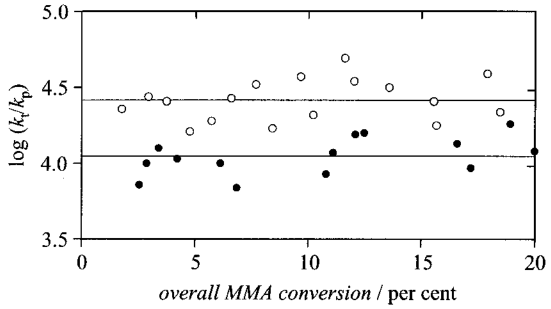

Figure 3. k_t/k_p of MMA bulk polymerizations at 40 °C and 1000 bar (open circles) and at 100 °C and 1000 bar (full circles) plotted against monomer conversion.

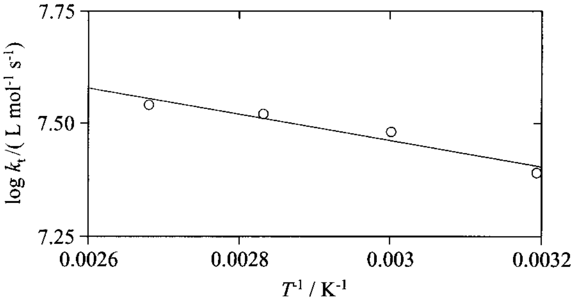

Figure 4. Arrhenius plot of k_t values for MMA bulk polymerizations at 40, 60, 80, and 100 °C and 1000 bar. Each data point is obtained as a mean value over an initial polymerization range extending up to about 20% monomer conversion (see Figure 3).

Table 2. Summary of Experimental k_t/k_p Values for MMA Bulk Polymerizations at Different Temperatures (T) and Pressures (p) (k_p Values Taken from Reference 10; k_t Calculated from k_t/k_p and k_p)

T/°C	p/bar	log(k_t/k_p)	log(k_p/L mol^{-1} s^{-1})	log(k_t/L mol^{-1} s^{-1})
40	1000	4.43	2.96	7.39
60	1000	4.32	3.16	7.48
80	1000	4.18	3.34	7.52
100	1000	4.03	3.51	7.54
60	1500	4.08	3.29	7.37

merizations at 1000 bar and temperatures ranging from 40 to 100 °C. In addition, for 60 °C a k_t/k_p value from a time-resolved experiment at a different pressure (1500 bar) is included.

With k_p being known from previous PLP–SEC studies,[10] k_t is easily available from k_t/k_p. The numbers for k_p and k_t are given in Table 2. k_t increases toward higher temperature and decreases toward higher pressure. An Arrhenius plot for k_t at 1000 bar is shown in Figure 4. The data are fitted by an Arrhenius line with an activation energy of $E_A(k_t) = 5.6 \pm 2.8$ kJ mol^{-1}.

The appreciable uncertainty in existing k_t data of MMA poses problems toward a comparison with our numbers. The entries for MMA k_t in the ref 27 vary by up to 2 orders of magnitude under ostensibly the same conditions. It is no suprise that, within this enormous range, agreement with our data is found. To afford for a more reasonable comparison, we decided to consider only the reported experimental k_t/k_p data and to derive k_t by implementing the IUPAC-recommended k_p values.[3] This strategy applied to the k_t/k_p data contained in refs 27 and 28 enormously reduces the scatter on k_t data from the literature. This can be seen from Figure 5, where the ambient pressure k_t data from literature (determined as just outlined) are plotted as open circles.

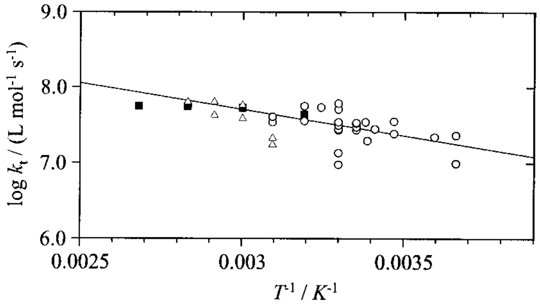

Figure 5. Comparison of k_t data derived from the literature[27,28] by a procedure described in the text (open circles) with experimental data from this study (filled squares). In addition, data from chemically initiated experiments (open triangles)[24] are shown. The straight line is obtained by only fitting k_t data from ref 27 and ref 28.

Fitting these literature values (open circles) yields the Arrhenius line in Figure 5. It needs to be noted that it is questionable for some of the literature k_t/k_p data whether k_t refers to a rate law as given in eq 2 or whether a termination rate expression has been used without the factor of 2. This uncertainty may give rise to differences in log k_t of 0.3 (logarithmic) units.

Using an activation volume of $\Delta V^{\#}(k_t) = 15 \pm 5$ cm^3 mol^{-1}, which is derived from the 1000 and 1500 bar experiments at 60 °C (see Table 2), our k_t values are extrapolated to ambient pressure. This procedure yields the full squares in Figure 5. It is gratifying to note that rather satisfactory agreement is found between our data and the literature values. It is not the intention of the present paper to provide critical evaluation of existing k_t data for MMA. This will be a forthcoming IUPAC activity after additional k_t material by several groups (including our own) will have become available. Figure 5 just wants to show that reasonable k_t values are derived by the new technique. Particularly noteworthy is the good agreement of k_t from the present investigation with recent values (open triangles) from chemically initiated MMA bulk polymerizations studied by Beuermann.[24] Agreement with k_t from PS–PLP experiments by the same author is, however, not obtained. In particular, the negative value of activation energy of k_t reported in ref 24 is not supported by our single pulse measurements.

It should be noted that the values of activation energy and activation volume of 5.6 ± 2.8 kJ mol^{-1} and 15 ± 5 cm^3 mol^{-1}, respectively, are close to the pressure-averaged activation energy of $E_A(k_t) = 6.2 \pm 3.3$ kJ mol^{-1} and to $\Delta V^{\#}(k_t) = 14.1 \pm 1.8$ cm^3 mol^{-1} (at 40 °C) recently deduced for styrene from PS–PLP experiments in the initial range of bulk polymerizations.[29] For both monomers, styrene and MMA, an extended initial conversion region is found where k_t is independent of the degree of monomer conversion.

It is beyond the scope of this paper to study k_t of MMA in any detail as a function of p and T. The present paper just wants to illustrate that, also for slowly propagating monomers, k_t may be derived from (modified) SP–PLP experiments. This finding allows for the extension of k_t studies to a wide variety of free-radical homo- and copolymerization systems in extended ranges of p, T, and monomer conversion. Part of this work is already underway in our laboratory. Upon further significant improvement of IR/NIR detection quality SP–PLP investigations into many detailed aspects, e.g., concerning a dependence of k_t on solvent type, polymer type and, in particular, on chain length, may be within reach even for the slowly propagating monomers.

Conclusions

SP−PLP experiments were performed on MMA to derive the ratio of termination to propagation rate coefficients, k_t/k_p. With k_p from PLP−SEC experiments, individual k_t for narrow ranges of monomer conversion, each extending over approximately 2%, is accessible. For the first time, SP−PLP experiments, associated with time-resolved spectroscopic measurement of polymerization induced by single laser pulses, have been performed on a slowly propagating monomer such as MMA.

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