*Macromolecules* **2003,** *36,* 9797−9803

# Application of Matrix-Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometry in Pulsed Laser Polymerization. Chain-Length-Dependent Propagation Rate Coefficients at High Molecular Weight: An Artifact Caused by Band Broadening in Size Exclusion Chromatography?

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*Received June 10, 2003; Revised Manuscript Received October 2, 2003*

ABSTRACT: The combination of matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-ToF-MS) and size exclusion chromatography (SEC) combined with pulsed laser polymerization has been used to evaluate propagation rate coefficients ($k_p$) in bulk free-radical polymerization for the systems methyl methacrylate and styrene. By varying laser frequencies, the relation between polymer chain length and observed propagation rate coefficient ($k_p^{obs}$) has been investigated in detail. It has been found that deviations between MALDI-ToF-MS and SEC at higher molecular weights are the result of instrumental effects in SEC. Moreover, using a model and taking into account experimental studies on the propagation of oligomeric species, it has been inferred that the relationship between $k_p^{obs}$ and polymer chain length is the result of chain-length-dependent behavior of the true $k_p$ in the oligomeric range, therewith excluding any chain-length-dependent behavior at higher molecular weights.

## Introduction

The knowledge of kinetic rate coefficients in polymerization is of paramount importance for modern production of polymers. Not only the rate of reaction of a polymerization is determined by the kinetics, but also the molecular weight distribution and, in copolymerization, the chemical composition distribution.

One of the most primary and important rate coefficients is the propagation rate coefficient ($k_p$). In most kinetic analysis a combination of $k_p$ and the termination rate coefficient ($k_t$) is determined. Knowledge of $k_p$ makes separation of both rate coefficients possible.

In 1986, a IUPAC working party entitled “Modeling of Free Radical Polymerization Kinetics and Processes” was founded which recommended the pulsed laser polymerization method in combination with size exclusion chromatography (PLP-SEC)[1−9] as the most reliable method for the determination of $k_p$[10−12] in radical polymerizations.

**Description of the Method.** The PLP-SEC technique was described originally by Genkin and Sokolov[1] and Alexandrov et al.[2] in 1977 and was further developed by Olaj et al. in 1987 and the years after.[3,9] This PLP method comprises the generation of radicals through a photoinitiator, dissociated by the light of a short laser pulse (~10 ns). The time of growth for a polymer chain is directly controlled by the time between pulses, and this experiment gives direct access to $k_p$.

The degree of polymerization for the chains initiated and terminated by short pulses of radicals induced by light (in combination with a photoinitiator) or radical-generating radiation like electron beams or $\gamma$-radiation is given by the simple equation[3]

$$L_{0,i} = ik_p[\mathrm{M}]t_p \qquad (1)$$

where $L_{0,i}$ is the chain length of the polymer formed in the process of growth in the time between two radical pulses, $t_p$ is the time between two subsequent radical pulses, and $i = 1, 2, 3, ....$ The higher order peaks ($i = 2, 3, ...$) may occur when growing chains survive termination by one or more subsequent pulses.

In between two pulses normal bimolecular termination can occur which is one of the sources for the so-called background polymer. Olaj et al.[3] suggested that the best measure of $L_{0,i}$ is the position of the inflection point (ip) at the low molecular weight side of the obtained PLP distribution analyzed by SEC.

A recent overview of all the publications where PLP−SEC has been used to obtain propagation rate coefficients contains over 100 references to the method.[13]

**Calibration of SEC.** Although the PLP/SEC method can result in accurate $k_p$ values, there are some problems. The method relies on accurate SEC calibration. If narrow molecular weight standards are not available, the method of universal calibration can be applied which again relies on the knowledge of the Mark−Houwink constants. One solution to this problem is the use of an in-line viscosity detector. The values for the Mark−Houwink constants are regularly updated resulting in updated $k_p$ values (e.g., Hutchinson et al.[14]).

Another issue is the extent of branching, in both the samples used for calibration and the actual PLP samples. This seems to be especially important for PLP experiments with acrylates.[15,16] Furthermore, simulations show that the extent of band broadening in SEC can affect the resulting $k_p$ values.[17,18]

An interesting method that is absolute in terms of molecular weight determination is matrix-assisted laser

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10.1021/ma034789k CCC: $25.00

desorption-ionization–time-of-flight–mass spectrometry (MALDI-ToF-MS). Danis et al.[19] were the first to investigate the molecular weight distribution of a polymer resulting from a PLP experiment with MALDI-ToF-MS. This was followed up in 1996 by Zammit et al.[20] and Schweer et al.[21] Interestingly enough, the findings by Schweer et al.[21] already indicated a big effect of column band broadening on the determination of $k_p$ prior to the simulations.[17,18]

Although very similar results were obtained with SEC and MALDI-ToF-MS, this method has not frequently been applied in combination with PLP. A reason for this might be that the intensity of the MALDI-ToF-MS signals is not representative for the amount of the particular polymer with that molecular weight; i.e., mass discrimination can occur.

**Chain-Length-Dependent $k_p$.** Recent results obtained with the PLP–SEC method by Olaj et al.[22,23] and in our lab[24] indicate that $k_p$ values do not seem to be independent of the frequency at which the results are obtained. This effect has been interpreted by Olaj et al. as a chain-length-dependent $k_p$ related to a change in local monomer concentration at the site of propagation.[22,23]

The surprising fact in these results is that the chain-length dependence extends to chain lengths well above the first few propagation steps. The latter chain-length dependence is well recognized and forms the reason that another method to determine $k_p$ values, electron spin resonance (ESR),[25] until recently rendered $k_p$ values inconsistent with the IUPAC values determined by PLP–SEC. The main reason for the differences between ESR and PLP is the high radical flux needed in the ESR experiment, rendering very short chains. It is known that the rate of propagation for the first propagation steps is higher than the long-chain limit,[26–28] and therefore ESR experiments usually gave higher values than PLP experiments. With this knowledge, the differences between the PLP and ESR method were resolved for styrene[29] and dodecyl methacrylate.[30]

In this paper the application of MALDI-ToF-MS in relation to instrumental issues in SEC and the chain length dependence of $k_p$ is investigated.

## Experimental Section

**Materials.** The monomers methyl methacrylate (MMA, Aldrich) and styrene (St, Aldrich) were purified from inhibitor by passing over a column with inhibitor remover (Aldrich, *tert*-butylcatechol remover for styrene, hydroquinone remover for MMA). The photoinitiator benzoin (Fluka, 99%) was used as received.

**Polymerizations.** The photoinitiator benzoin was added to the monomer to a concentration of 7.5 mM. The solution of photoinitiator in monomer was purged with argon for at least 20 min in order to remove oxygen. Pulsed laser polymerization experiments were carried out using a Lambda Physics LPX110iMC excimer laser operating at the XeF line (351 nm) with a pulse width of 20 ns. The monomer mixture is placed in a thermostated quartz glass cell that is completely irradiated by the laser beam. The temperature is measured inside the thermostated cell using a thermocouple. Laser repetition rates were varied between 0.5 and 100 Hz, whereas the laser energy directly measured at the laser exit was set at a constant level of 50 mJ/pulse. Temperatures at which polymerization was carried out were in the range of −20 to 25 °C for MMA and 20 to 60 °C for styrene. Samples were exposed to the pulsed laser beam for 90 s up to 10 min to allow polymerization. After isolation of the sample, small amounts of hydroquinone or 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) were added to MMA and styrene, respectively, in order to prevent further polymerization. After evaporation of residual monomer under reduced pressure, using a high-vacuum pump, conversions were determined by gravimetrical analysis, and obtained conversions were well below 3%. For the calculation of the densities of styrene[31] and MMA,[32] the following formulas were used

$$d_{\mathrm{St}} = 0.9236 - 8.87 \times 10^{4} T$$

$$d_{\mathrm{MMA}} = 0.9569 - 1.2129 \times 10^{-3} T + 1.6813 \times 10^{-6} T^2 - 1.0164 \times 10^{-8} T^3$$

where $d$ is given in g mL$^{-1}$ and $T$ is the temperature in °C.

**Analysis.** MALDI-ToF-MS analysis was carried out on a Voyager DE-STR from Applied Biosystems. The matrix is *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), which was synthesized according to literature procedures.[33] Sodium trifluoroacetate (Aldrich, 98%) and silver trifluoroacetate (Aldrich, 98%) were added to pMMA and pSt, respectively, as cationization agents. The matrix was dissolved in THF at a concentration of 40 mg mL$^{-1}$. Salt was added to THF at typical concentrations of 1 mg mL$^{-1}$. Polymer was dissolved in THF at approximately 1 mg mL$^{-1}$. In a typical MALDI-ToF-MS analysis the matrix, salt and polymer solution were premixed in a ratio of 10:1:5. The premixed solutions were handspotted on the target well and left to dry. All spectra were recorded in the linear mode. For a correct interpretation of MALDI-ToF-MS mass spectra, peaks were integrated in the mass domain[34] over the monomer repetition unit. To minimize spot-to-spot variation, two or three separate spectra, recorded from different spots, consisting of 2000–5000 individual shots each, were used for the calculation of $k_p$. Peak maxima were evaluated from the intersection of the first derivative with the *x*-axis obtained after cubic spline smoothing of the integrated data. The spectra shown in this article were corrected for the fact that acquisition is carried out in the time domain and not in the mass domain.[34]

SEC analysis was carried out on a Viscotek Triple-SEC setup consisting of a Gynkotek pump and four mixed-B columns (Polymer Laboratories) with THF (Biosolve, Ar-stabilized, 99.8%) as solvent running at 1.0 mL min$^{-1}$. Calibration curves were constructed using both pSt (molar mass range from 580 to $1 \times 10^6$ g mol$^{-1}$) and pMMA (molar mass range from 650 to $1.5 \times 10^4$ g mol$^{-1}$) standards (Polymer Laboratories) of narrow polydispersity. For evaluation of the molecular weight distributions the differential refractive index was used as a concentration detector for both systems. The polymer was dissolved in THF at typical concentrations of 2 mg mL$^{-1}$.

## Results and Discussion

**Propagation Rate Coefficients by MALDI-ToF-MS.** The use of MALDI-ToF-MS in the analysis of polymer distributions has gained a lot of interest in the past years. Issues like correct interpretation of MALDI-ToF-MS signals[34,35] and the use of MALDI-ToF-MS in broad distributions are debated in numerous articles.[36–41]

One issue in PLP experiments analyzed with MALDI-ToF-MS is the best measure for $k_p$. Although usually the inflection point in a logarithmic weight distribution resulting from SEC analysis is taken, the distribution resulting from a MALDI-ToF-MS analysis is a (discrete) number molecular weight distribution (nMWD). In 1996, Buback et al.[17] already described that when working at high initial radical concentrations (the so-called high termination rate limit (HTRL), a term introduced by Sarnecki et al.[42]), $k_p$ can be estimated reliably from the peak maximum in a number molecular weight distribution within 2% accuracy. To investigate whether under the HTRL conditions peak maxima can be used reliably to calculate $k_p$ over a wide range of laser

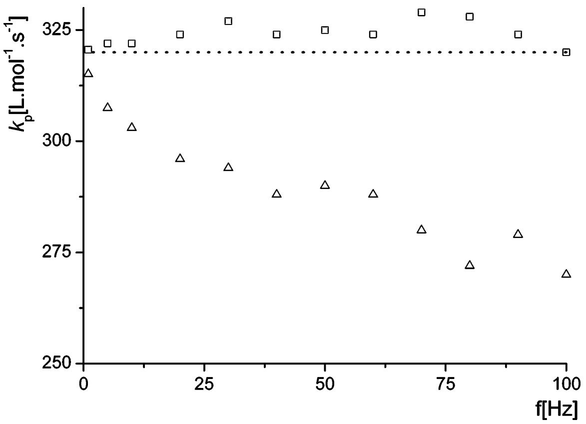

**Figure 1.** Dependence on laser frequency of $k_p$ values derived from peak maximum (□) and inflection point (△) from a nMWD compared to the input value for the simulation (- - -). The nMWDs are obtained by Monte Carlo simulations for MMA (termination by disproportionation) using laser frequencies varying from 1 to 100 Hz. Input for Monte Carlo simulation: $k_p = 320$ L mol$^{-1}$ s$^{-1}$, $k_{t(i,j)} = 2 \times 10^8 (i.j)^{-(0.2)/2}$ L mol$^{-1}$ s$^{-1}$, [M] = 10 M, [R$_0$] = 5 × 10$^{-6}$ M.

frequencies, Monte Carlo simulations of PLP experiments based on the algorithm by O'Driscoll et al.[43] have been carried out. From the simulated nMWDs both peak maxima and inflection points were used to calculate $k_p$ values and compared to the simulation input value (Figure 1). It is clearly demonstrated that over a whole range of laser frequencies the $k_p$ value can be reliably estimated within 3% accuracy from the peak maximum in a nMWD. For $k_p$ values determined from the inflection point systematic deviations up to 15% are found at the higher repetition rates.

Another issue that needs to be addressed is whether mass discrimination in MALDI-ToF-MS can influence the position of the peak maximum in a MWD obtained by PLP experiments. From the past it is known that when dealing with broad distributions (as a general rule polydispersity index (PDI) > 1.2),[37] mass discrimination can have a serious effect on the distribution and peak maximum. Any form of discrimination will therefore also affect the distribution obtained from a PLP experiment. In our experience, the selected matrix DCTB is showing much less mass discrimination effects than previously used matrices like dithranol or dihydroxybenzoic acid (DHB).[44] Furthermore, the characteristic peaks that are the result of PLP experiments usually have the characteristics of very narrow Gaussian distributions (PDI < 1.2, see Figure 2). For these narrow Gaussian distributions it is generally accepted that mass discrimination effects have a negligible influence on the peak position. Therefore, MALDI-ToF-MS can be used in a reliable way for $k_p$ determination, especially when peak maxima can be used as is indicated in Figure 1.

PLP experiments were carried out using the monomers methyl methacrylate and styrene with temperatures chosen as such that with a wide range of laser frequencies peak positions could be obtained ranging from low to high masses. Figure 2 gives a good impression of the type of distributions obtained, with clearly resolved first-order peaks shifting to higher molecular weights with decreasing laser frequency. It can also be observed that at the higher frequencies (Figure 2, 50 Hz), overlap is occurring between first-order and higher-order peaks, resulting in tailing to the higher masses. For the calculation of propagation rate coefficients, peak maxima from the nMWD were determined using MALDI-ToF-MS, whereas inflection points from the logarithmic MWD were determined using SEC. In the interpretation of the propagation rate coefficient it should be realized that, as already stated by Nikitin et al.,[45] Kaminsky et al.,[46] and Olaj et al.,[23] in the case of chain-length-dependent propagation rate coefficients the observed propagation rate coefficient is a summation of all individual propagation steps ($n$) as described by eq 2

$$\frac{1}{k_p^{\mathrm{obs}}(n)} = \frac{1}{n}\sum_{i=1}^{n}\frac{1}{k_p(i)} \qquad (2)$$

The use of MALDI-ToF-MS allows for the exact determination of polymeric masses and therefore the determination of the number of propagation steps ($n$) from the polymeric chain length ($L$) according to

$$n = L - p \qquad (3)$$

where $p$ equals 1 in the case of termination by disproportionation (MMA) and 2 in the case of termination by combination (St).

**Observed Propagation Rate Coefficients ($k_p^{\mathrm{obs}}$): MALDI-ToF-MS vs SEC.** In Figure 3 $k_p^{\mathrm{obs}}$ is presented

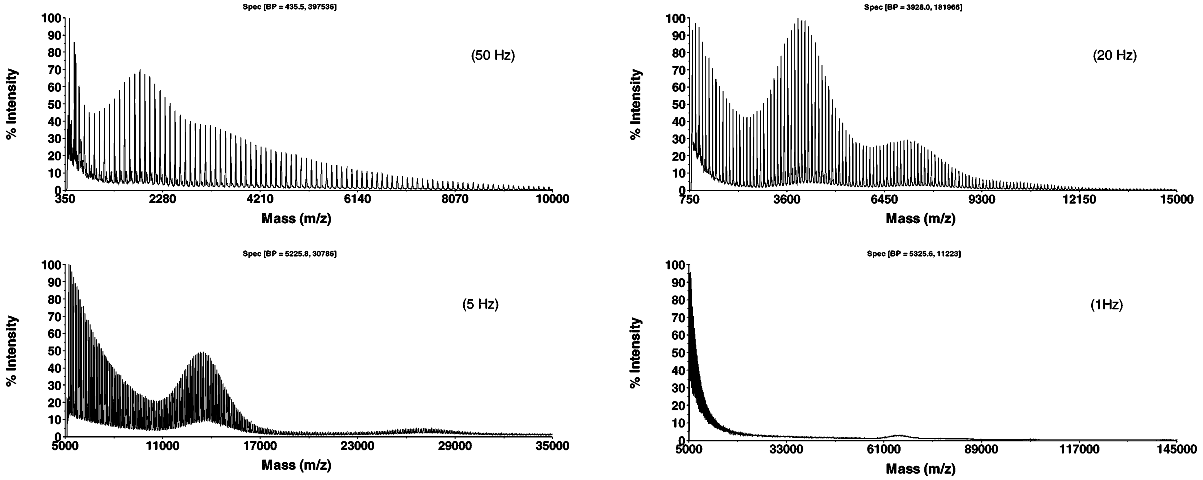

**Figure 2.** Some examples for MALDI-ToF-MS spectra from PLP-experiments obtained for methyl methacrylate bulk polymerization at −18.3 °C varying the laser frequency from 50 Hz down to 1 Hz. MALDI-ToF-MS mass spectra for styrene are included in the Supporting Information.

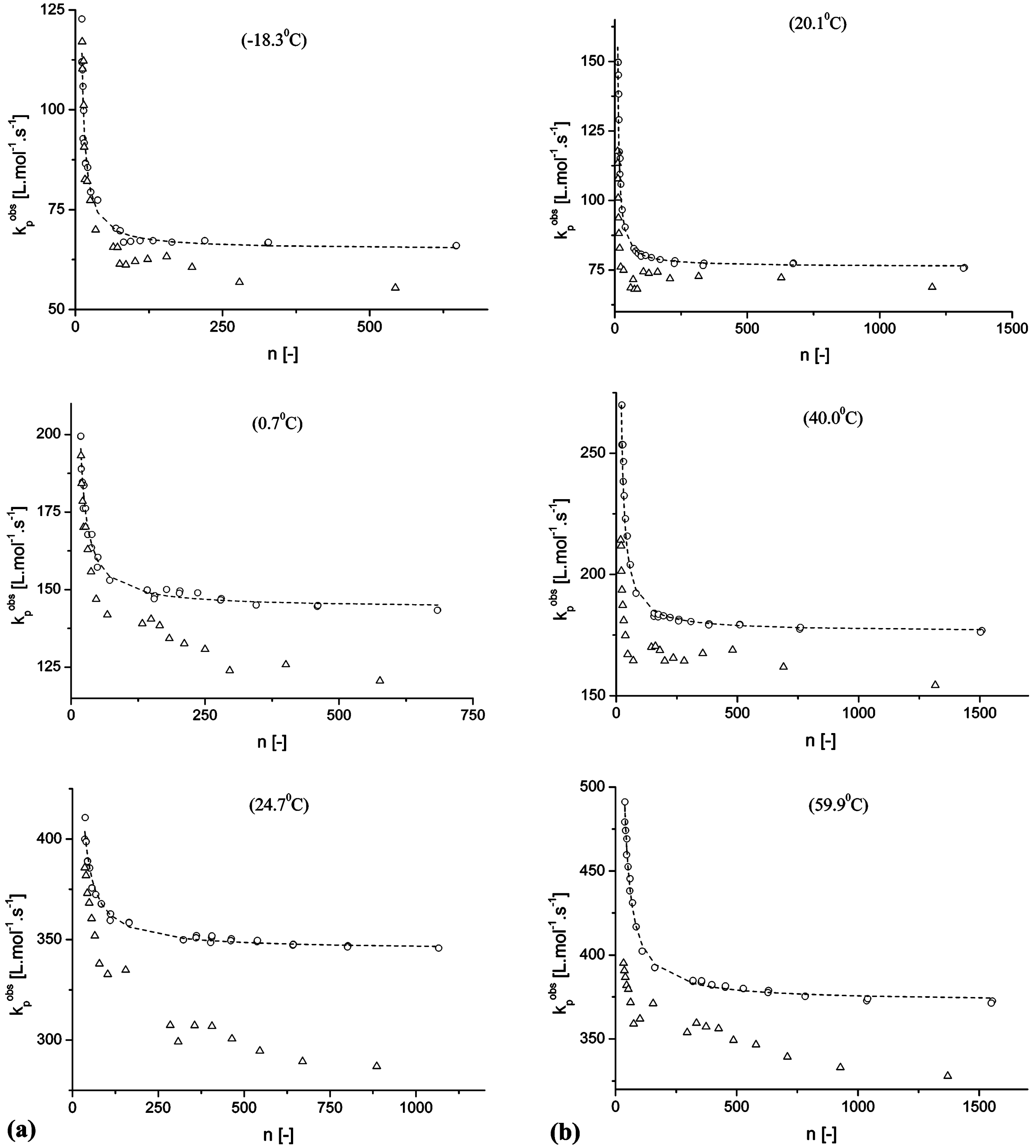

**Figure 3.** Experimentally observed propagation rate coefficients ($k_p^{obs}$) vs number of propagation steps ($n$) in bulk for MMA (a) and styrene (b) derived from the first peak maximum in MALDI-ToF-MS (○) and the first inflection point from SEC (△). The best fits according to eq 4 (- - -) for the MALDI-ToF-MS data are indicated with the parameters given in Table 1.

as a function of the number of propagation steps ($n$) as measured by MALDI-ToF-MS (○) and by SEC (△) for MMA (Figure 3a) and styrene (Figure 3b). An interesting fact is revealed when comparing the results of the two different analytical techniques at the higher number of propagation steps. Whereas $k_p^{obs}$ as measured by SEC decreases with increasing chain length, thus confirming the observations as previously found by Olaj et al.,[22,23] the $k_p^{obs}$ in MALDI-ToF-MS has already reached its long-chain limit value within 5% accuracy before 100 propagation steps have occurred. The fact that the observed propagation rate coefficient is almost constant after the first 100 propagation steps is therefore very strong evidence that any chain-length-dependent behavior is limited to the lower chain-length regions. At the lower number of propagation steps both analytical techniques show higher observed propagation constants, thus confirming results obtained by ESR experiments under high radical fluxes.[29]

The differences between MALDI-ToF-MS and SEC at higher molecular weights can have different origins. First of all, it has to be realized that $k_p$ values determined by MALDI-ToF-MS and SEC originate from different positions in different distributions. By simulations[17] it has already been shown that the peak maximum from an nMWD is found at higher chain lengths than the inflection point in a logarithmic MWD. The fact that the differences between SEC and MALDI-ToF-MS increase with an increasing number of propagation steps suggests that there is another mechanism at work. SEC suffers from two major disadvantages. First of all, it is not an absolute technique; e.g., for the calibration

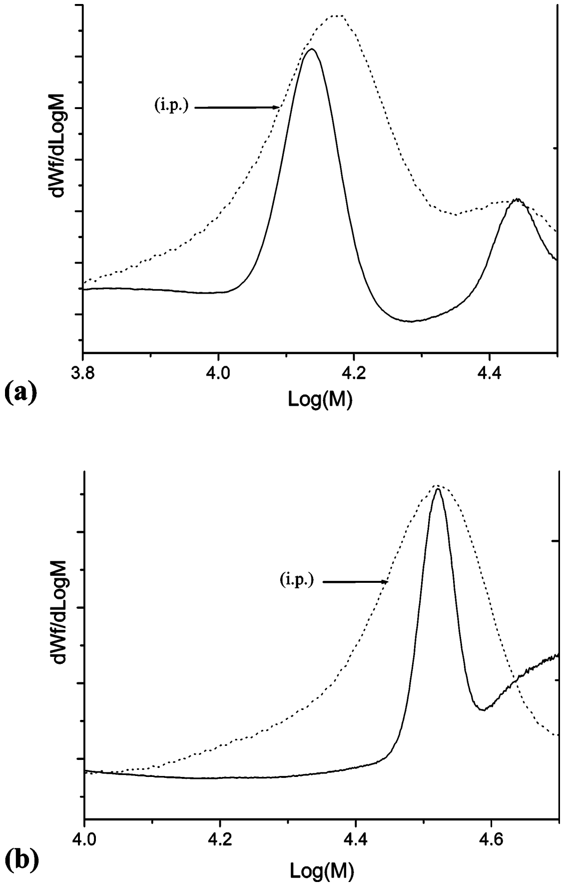

**Figure 4.** Overlay of logarithmic MWD obtained from SEC (- - -) and calculated from a MALDI-ToF-MS nMWD distribution (—) for MMA at two different laser frequencies: (a) $f = 5$ Hz and (b) $f = 2$ Hz. The arrows indicate the inflection points in the logarithmic MWD obtained by SEC.

to be carried out correctly, one needs to rely on the molecular weight values of narrow standards as supplied by the manufacturer. Furthermore, it is a well-known fact that SEC suffers from band broadening effects.[47] The effect of column band broadening can result in an overestimation of the PDI of narrow polymer distributions.[48,49] As a result of this, the difference between the true inflection point and the observed inflection point for narrow distributions increases with molar masses increasing. Obviously, the same effect will also play a role in PLP-generated polymer distributions. To visualize the differences between MALDI-ToF-MS and SEC, Figure 4a,b provides two distributions for MMA at the higher molecular weights, where the integrated MALDI-ToF-MS mass spectrum has been converted to a logarithmic MWD, using the definitions by Shortt.[50] In doing so, one has to realize that at the very high molecular weights MALDI-ToF-MS mass spectra are very sensitive to baseline problems and low signal-to-noise ratios. Converting MALDI-ToF-MS mass spectra to logarithmic MWDs therefore enhances these effects.

The main focus of Figure 4a,b therefore should lie on the shape and position of the PLP peak, for which it can easily be seen that calibration effects can have some influence on the position of the peak (Figure 4a), but broadening in general will result in an underestimation of the inflection point that is increasing with increasing chain length (Figure 4a,b). These observations are in agreement with experimental observations by Schweer et al.[51] and simulations of PLP dealing with column band broadening recently carried out by Beuermann.[18] For a good understanding of the concept of column band broadening, MALDI-ToF-MS may be a valuable tool since broadening effects in MALDI-ToF-MS are insignificant. Comparison between MALDI-ToF-MS and SEC should therefore be carried out for standards with low PDIs for which mass discrimination effects, baseline correction, and signal-to-noise ratio should pose no problems.

**Observed $k_p$ vs "True" $k_p$.** Knowing that the observed propagation rate coefficient is nothing but a summation of all the individual propagation steps that have taken place at lower chain lengths (eq 2), it is tempting to extract information about the 'true" propagation rate coefficient from the observed propagation rate coefficient. Using transition-state theory, it has already been shown that going from monomeric radical species to the corresponding macro radical, propagation rate coefficients may change by a factor of 10−25.[52] From experimental time-resolved infrared spectroscopy, it is also known that photoinitiation can be accompanied by very high initiation rate coefficients ($k_i$) that are several orders of magnitude larger than the subsequent propagation rate coefficients.[53] In 1992, Moad et al.[27] showed by performing nitroxide-trapping experiments that indeed the first two propagation rate coefficients are an order of magnitude larger than the long-chain propagation rate coefficient. Gridnev et al.[26] later on published supporting evidence for this behavior with the use of catalytic chain transfer experiments. All these articles support the observation that indeed chain-length-dependent behavior is found in the oligomeric range. So far, however, no theoretical model has been developed that is able to describe the chain-length dependence of $k_p$ in the oligomeric range. We therefore introduce a simplified model in which the minimum number of propagation steps ($i_{min}$), deviating from the long-chain limit ($k_p(\infty)$) can be estimated. In this simplified model a minimum number of propagation steps including the initiation step (under these definitions $k_p(1) = k_i$) are assumed infinitely fast compared to the subsequent ($n > i_{min}$) propagation steps. Under these conditions eq 2 is readily transformed into

$$k_p^{obs}(n) = \frac{n}{n - i_{min}}\, k_p(\infty) \qquad (4)$$

in which $k_p(\infty)$ is a constant propagation rate coefficient for any radical having a chain length larger than ($i_{min} + 1$). Equation 4 has been used to fit the results as obtained by the MALDI-ToF-MS analysis by nonlinear least-squares analysis.[54,55] Because small deviations at low chain lengths can result in large deviations in the measured $k_p^{obs}$, it was assumed that peak maxima in MALDI-ToF-MS could be obtained with an accuracy of 2 repeat units at the lower masses, with a limit of 1% accuracy at the higher masses. The nonlinear least-squares fits have been included in Figure 3a,b (dashed lines), whereas the values for these best fits are also included in Table 1.

A striking result from the fits of eq 4 is revealed when inspecting Table 1. Although $k_p^{obs}$ decreases up to a chain length of 100 units, this can be completely accounted for by a chain-length-dependent behavior of the "true" $k_p$ limited toward the oligomeric range ($i_{min} \approx 5-9$). The model used to fit the data is based on the assumption that the first $i_{min}$ propagation steps are

**Table 1. Values of Parameters of Nonlinear[54,55] Fits According to Eq 4 for Methyl Methacrylate and Styrene at Different Temperatures[a]**

| MMA | | | styrene | | |
|---|---|---|---|---|---|
| $T$ [°C] | $k_p(\infty)$ [L mol$^{-1}$ s$^{-1}$] | $i_{min}$ | $T$ [°C] | $k_p(\infty)$ [L mol$^{-1}$ s$^{-1}$] | $i_{min}$ |
| −18.3 | 65.6 ± 0.6 | 5.2 ± 0.7 | 20.1 | 76.0 ± 0.6 | 5.7 ± 0.6 |
| 0.7 | 144.2 ± 1.1 | 4.9 ± 0.9 | 40.0 | 175.9 ± 1.3 | 7.3 ± 0.9 |
| 24.7 | 345.4 ± 2.5 | 5.1 ± 1.1 | 59.9 | 372.2 ± 2.6 | 9.1 ± 1.2 |

[a] The variances indicated refer to 95% confidence intervals, using a nonlinear least-squares approach in which the weighing of the data was performed by an individual weighing scheme.[54,55] The 95% joint confidence interval was constructed using the $\chi^2$ distribution.[54,55] The absolute errors in the measured chain length ($L$) were transposed to an error in $k_p$, for which it was assumed that peak maxima could be obtained with an accuracy of 2 repeat units at the lower masses with a limit of 1% accuracy at the higher masses.

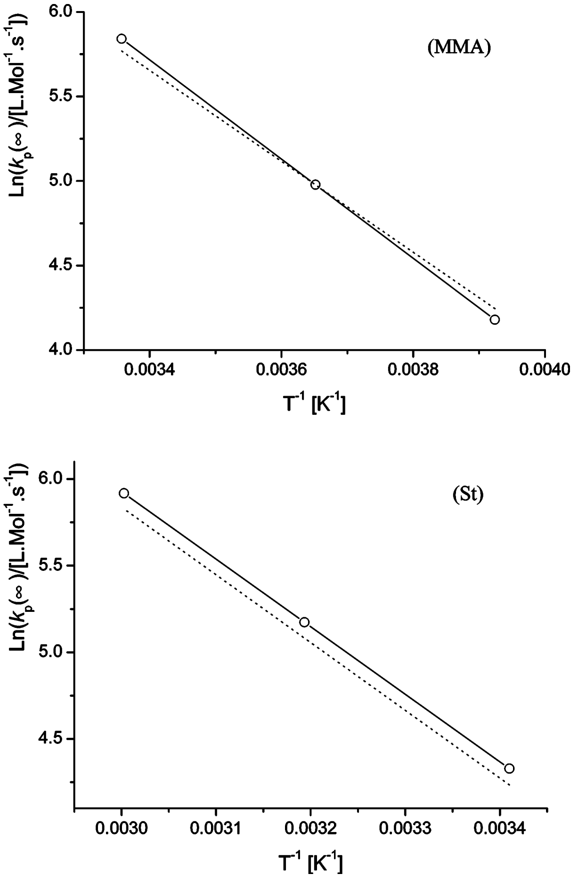

**Figure 5.** Arrhenius plots for $k_p(\infty)$ values derived from eq 4 for methyl methacrylate (MMA) and styrene (St). Indicated are the linear fits (—) and IUPAC benchmark values (- - -).

infinitely fast, which is not the case in reality. However, if it is assumed that $k_p$ is constant after ($i_{min}$ + 1) propagation steps, and assuming that the initiation step is infinitely fast, the subsequent 5−9 propagation steps on average only have to be 5−9 times as fast compared to the constant $k_p$, which again is in agreement with experimental evidence.[26,27] It is therefore believed that any chain-length dependence of the "true" propagation rate coefficient is limited to the first 10 propagation steps.

Now that new long-chain values have been established for $k_p$ using the new PLP-MALDI-ToF-MS method, these results can be compared to the IUPAC benchmark values published for both styrene[56] and MMA.[57] For both monomers Arrhenius plots were constructed (Figure 5) using the obtained $k_p(\infty)$ values displayed in Table 1. The IUPAC benchmark values for the Arrhenius parameters are in good agreement with the newly obtained Arrhenius parameters for styrene (see Table 2), whereas differences are found for MMA. Comparison of the obtained Arrhenius plots, however, reveals that for both systems the differences at the investigated temperatures between this work and the IUPAC values are small.

**Table 2. Frequency Factor ($A$) and Activation Energy ($E_{act}$) for Styrene and Methyl Methacrylate Calculated by Using the Values for $k_p(\infty)$ Derived from Eq 4 Compared to IUPAC Values[5657]**

| | this work | | IUPAC | |
|---|---|---|---|---|
| | $A/10^6$ | $E_{act}$ [kJ mol$^{-1}$] | $A/10^6$ | $E_{act}$ [kJ mol$^{-1}$] |
| MMA | 6.52 | 24.4 | 2.67 | 22.4 |
| styrene | 45.1 | 32.4 | 42.7 | 32.5 |

## Conclusion

Just like the introduction of the IUPAC recommended method of pulsed laser polymerization in combination with size exclusion chromatography resulted in the determination of reliable propagation rate coefficients, it was just a matter of time before its limitations were to be revealed. The combination of pulsed laser polymerization and MALDI-ToF-MS has been shown to be less sensitive to inaccuracies in the determination of the MWD than PLP-SEC. This has led us to conclude that previously observed chain-length-dependent $k_p$ values at high chain lengths are the result of column band broadening effects in SEC. Moreover, it has been demonstrated that using the PLP-MALDI-ToF-MS method enables one to extract detailed information on the chain-length-dependent behavior of the observed propagation rate coefficient for both MMA and styrene. From the observed propagation rate coefficient it has been deduced that the chain-length dependence of the "true" propagation rate coefficient is limited to the first 10 propagation steps.

**Supporting Information Available:** Examples of MALDI-ToF-MS mass spectra for styrene and tables with the numerical values from Figure 3a,b. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA034789K