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Copolymerization Kinetics of Methyl Methacrylate−Styrene Obtained by PLP-MALDI-ToF-MS

Robin X. E. Willemse and Alex M. van Herk*

Contribution from the Laboratory of Polymer Chemistry, Department of Chemical Engineering, Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven, The Netherlands

Received December 8, 2005; E-mail: A.M.v.Herk@tue.nl

Abstract: The combination of MALDI-ToF-MS and pulsed laser polymerization has been used to study the propagation rate coefficients for the copolymer system styrene−methyl methacrylate. For the first time, complete information regarding mode of termination, reactivity of photoinitiator-derived radicals, copolymer molecular mass, chemical composition, and copolymerization rates is obtained interrelated. The polymerizations were carried out in bulk with varying styrene concentrations at a temperature of 15.2 °C by an excimer pulsed laser with varying frequencies. Both chemical composition distributions and molecular weight distributions were determined by MALDI-ToF-MS. The data were fitted to the implicit penultimate unit model and have resulted in new point estimates of the monomer and radical reactivity ratios for the copolymer system styrene−methyl methacrylate: $r_{\mathrm{St}} = 0.517$, $r_{\mathrm{MMA}} = 0.420$, $s_{\mathrm{St}} = 0.296$, $s_{\mathrm{MMA}} = 0.262$. Comparison between Monte Carlo simulations and the obtained results further confirmed the very successful combination of pulsed laser copolymerization experiments with MALDI-ToF-MS. The obtained results are believed to be the most accurate and complete set of copolymerization parameters to date.

Introduction

Many studies in the past have been devoted to describing copolymerization kinetics. One of the earliest models capable of describing copolymerization kinetics, chemical composition, and sequence distribution is known as the terminal model (TM) and was introduced in 1944.[1,2] However, soon after its introduction, copolymerization systems were observed for which the TM failed to describe copolymerization kinetics. With the introduction of pulsed laser polymerization in the 1980s, the number of systems that was deviating from TM kinetics increased rapidly.

To account for the discrepancy found in the kinetics, new models were developed, of which the penultimate unit model[3] (PUM) is perhaps the best known and most applied currently. The difference between the TM and the PUM is related to the considerable influence that a penultimate unit may exert on the terminal unit thus influencing the reactivity of the terminal radical and therefore its kinetics. Aspects of both models are detailed elsewhere and are not restated here.

Most studies related to the determination of copolymerization kinetics require two different steps, e.g., (i) determination of a Mayo−Lewis[1] plot by, for example, ^{1}H NMR, and (ii) determination of the average propagation rate coefficients using pulsed laser polymerization in combination with size exclusion chromatography. In this article, a new method is proposed which allows for the determination of both a Mayo−Lewis plot and average propagation rate coefficients from one series of PLP experiments using MALDI-ToF-MS. The major advantages of using MALDI-ToF-MS in the analysis of the copolymers are that not only unbiased information on molar mass is obtained (without problems associated with column broading as in size exclusion chromatography) but also information about end-groups and chemical composition of the copolymer chains is obtained. The model system styrene−methyl methacrylate has been chosen as this copolymerization system has been studied extensively in the past and therefore allows for easy testing of the proposed method. MALDI-ToF-MS will be used as a tool to study chemical composition data, average propagation kinetics, and copolymer chemical composition distributions. The results of this study are then finally compared to Monte Carlo simulations.

Experimental Section

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

Polymerization and Polymer Analysis. Benzoin was added to the polymerization mixtures at concentrations of approximately 5×10^{-3} mol L^{-1}. Prior to the pulsed laser polymerization experiments, the polymerization mixtures were subjected to three freeze−pump−thaw cycles to remove dissolved oxygen. For each feed composition, two PLP experiments were carried out using laser energies of 40 and 60 mJ pulse^{-1} at a reaction temperature equal to 15.2 °C. This temperature was chosen to have optimal cooling capacity related to the temperature of the cooling water. A complete description of the setup can be found

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(1) Mayo, F. R.; Lewis, F. M. *J. Amer. Chem. Soc.* **1944**, *66*, 1594−1601.
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elsewhere,[4] whereas further experimental conditions can be found in Table 3. The polymers were isolated from the reaction mixture by evaporating the nonreacted monomer in a high-vacuum stove. Conversions were determined by gravimetrical analysis and were well below 1%.

MALDI-ToF-MS analysis was carried out on a Voyager DE-STR from Applied Biosystems. The matrix used for the analysis was *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) which was synthesized according to literature procedures.[5] The matrix was dissolved in THF at a concentration of 40 mg mL^{-1}. Potassium trifluoracetate (Aldrich, 98%) was used as a cationization agent and was added to THF at typical concentrations of 1 mg mL^{-1}. The polymer was dissolved in THF at approximately 2 mg mL^{-1}. In a typical MALDI-ToF-MS experiment, the matrix, salt, and polymer solution was premixed in a ratio of 10:1:5. The premixed solutions were handspotted on the target-well and left to dry. Mass spectra were analyzed in the linear and the reflector modes. One spectral analysis consists of a coaddition of approximately 5000 individual laser shots. Mass spectra obtained in the linear mode were integrated over the average monomer repeat unit. Peak maxima were evaluated from the intersection of the first derivative with the mass axis, obtained after a cubic spline smoothing of the integrated data. Mass spectra obtained in the reflector mode were baseline corrected using the advanced baseline correction from the DataExplorer software and interpreted using self-developed algorithms in a home-written program.[6,7]

The average monomer concentration was determined according to

$$[M]_{\mathrm{avg}} = f_{\mathrm{St}}[M]_{\mathrm{St}} + (1 - f_{\mathrm{St}})[M]_{\mathrm{MMA}} \qquad (1)$$

where $[M]_{\mathrm{St}}$ and $[M]_{\mathrm{MMA}}$ are the monomer concentrations of styrene and methyl methacrylate, respectively, and f_{St} is the monomer feed composition of styrene. The respective monomer densities of styrene[8] and MMA[9] were calculated using

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

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

where d is given in g mL^{-1} and T is the temperature in °C. For the calculation of this average monomer concentration, it is assumed that there is no volume contraction during the low-conversion polymerization experiments.

For the determination of the characteristic chain length, $L_{0,1}$, evaluated from the peak maximum in a MALDI-ToF-MS mass spectrum, the following equation was used:

$$L_{0,1} = \frac{M_{\mathrm{peak\ maximum}}}{F_{\mathrm{St}} M_{\mathrm{St}} + (1 - F_{\mathrm{St}}) M_{\mathrm{MMA}}} \qquad (2)$$

where M_{St} and M_{MMA} are the respective monomer masses and F_{St} is the respective copolymer composition of styrene. The latter was evaluated using eq 6 and the monomer reactivity ratio data as determined in this manuscript.

Results and Discussion

Previously, we have demonstrated the use of MALDI-ToF-MS in elucidating copolymer microstructure and average chemical composition with the use of a copolymer fingerprint analysis.[6,7]

It was shown in our lab that the combination of the matrix and the (co)polymer can be optimized for the MALDI-ToF-MS not to suffer from extensive mass discrimination when obtaining full copolymer mass distributions.[4,6,7]

The proposed analysis of copolymer mass spectra requires the knowledge of possible endgroups ($\mathrm{E_I}$ and/or $\mathrm{E_{II}}$) and relates these to the chemical composition (n_{i} and m_{j}) of the copolymer via

$$m_{\mathrm{theor}} = n_{\mathrm{i}} M_{\mathrm{i}} + m_{\mathrm{j}} M_{\mathrm{j}} + \mathrm{E_I} + \mathrm{E_{II}} + M^{+} \qquad (3)$$

in which M_{i} and M_{j} are the masses of the monomer units i and j and M^{+} is the mass of the cationization agent. Good knowledge of endgroups that might occur is of paramount importance for a successful analysis of the copolymer mass spectra. When the system styrene–methyl methacrylate is considered, three different types of chains may be present in the mass spectrum due to differences in the mode of termination. For methacrylates, it is known that disproportionation is the dominant bimolecular termination reaction, whereas in the case of styrene, this is predominantly termination by combination.[10] For a copolymerization reaction, the overall mode of termination may thus be a combination of the two modes of termination for which the contribution of either one of the modes of termination can change with a variation of the monomer feed composition.

The second difficulty that is met in pulsed laser polymerization experiments is the use of a photoinitiator. As photoinitiators of Norrish type II are asymmetrical, two different types of initiating species are present, differing in mass. This combined with the two termination modes may lead to up to seven different copolymer species present in a mass spectrum. In this view, the choice of the photoinitiator benzoin is an important one because it consists of two different radicals which differ by only 2 g mol^{-1} in mass, e.g., a benzoyl radical and a benzyl alcohol radical, further denoted as radical A and B, with masses $M_{\mathrm{A}} = 105.12$ g mol^{-1} and $M_{\mathrm{B}} = 107.13$ g mol^{-1}, respectively. From single-pulse pulsed laser polymerization experiments, analyzed by MALDI-ToF-MS, it can be shown that in the case of benzoin the benzoyl radical is the more reactive radical which may greatly reduce the complexity of the resulting mass spectra.[11]

In Figure 1, an expanded part of the MALDI-ToF-MS mass spectra is shown for a PLP reaction carried out at low styrene content ($f_{\mathrm{St}} = 0.053$). Indicated by the arrows are several possible peak assignments with the endgroups A and B, for which the theoretical masses are collected in Table 1. The systematic differences that can be observed between the theoretical and experimental masses stem from spot-to-spot variations in a MALDI-ToF-MS measurement. From the isotopic pattern in Figure 1, three observations can be made:

(1) Several peaks are present which may be explained by more than one unique combination of monomer units, endgroups, and mode of termination.

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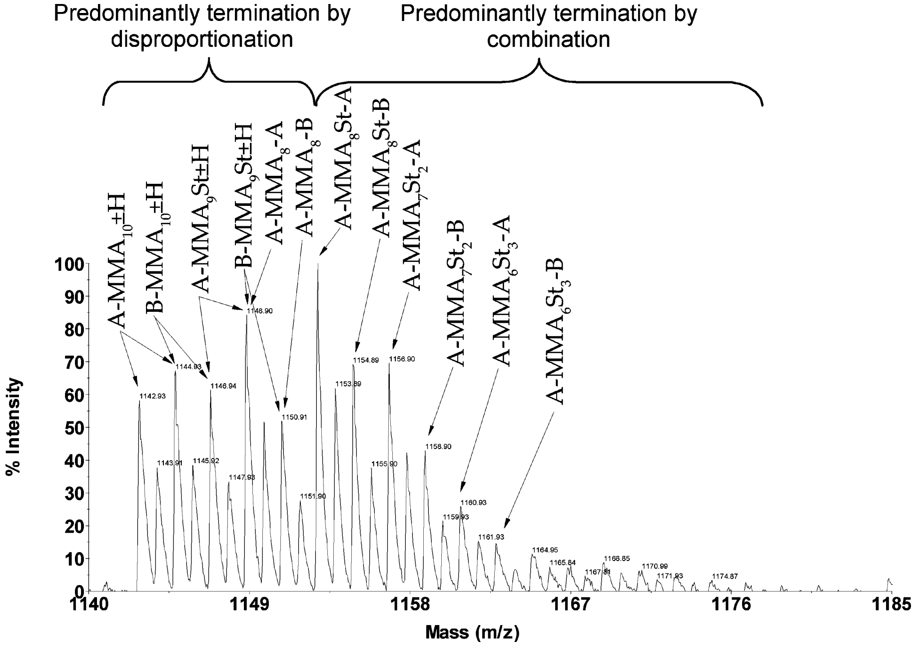

Figure 1. Expanded section of a MALDI-ToF-MS mass spectrum obtained via bulk pulsed laser copolymerization of methyl methacrylate and styrene using benzoin as a photoinitiator. The polymerization was carried out with a pulse frequency of 8 Hz at a styrene feed composition of $f_{St} = 0.053$. Two distinct regions are depicted in which polymer chains are present which are predominantly the result of termination by disproportionation or combination, respectively. Peak assignments are given in which A and B refer to the benzoyl or benzyl alcohol radical, respectively. In Table 1 the theoretical and experimental masses have been collected.

Table 1. Experimental and Theoretical Masses for the Assigned Peaks Shown in Figure 1[a]

termination by disproportionation			termination by combination		
formula	m/z_{exptl} [g mol^{-1}]	m/z_{theor} [g mol^{-1}]	formula	m/z_{exptl} [g mol^{-1}]	m/z_{theor} [g mol^{-1}]
A−MMA$_{10}$ ± H	1142.88/1144.89	1143.51/1145.53	A−MMA$_9$−A	1148.88	1149.50
B−MMA$_{10}$ ± H	1144.89/1146.89	1145.53/1147.55	A−MMA$_9$−B	1150.89	1151.52
A−MMA$_9$−St ± H	1146.89/1148.88	1147.52/1149.54	A−MMA$_8$−St−A	1152.86	1153.51
A−MMA$_9$−St ± H	1148.88/1150.89	1149.54/1151.56	A−MMA$_8$−St−B	1154.88	1155.53
			A−MMA$_7$−St$_2$−A	1156.88	1157.52
			A−MMA$_7$−St$_2$−B	1158.89	1159.54
			A−MMA$_6$−St$_3$−A	1160.89	1161.53
			A−MMA$_6$−St$_3$−B	1162.90	1163.55

[a] The endgroups A and B refer to the benzoyl and benzyl alcohol radical, respectively.

(2) Introducing approximately 5% of styrene changes the bimolecular termination reaction from predominantly disproportionation to a considerable contribution of termination by combination. This can be rationalized in the following way. Using the terminal model, we can make an estimation of the ratio of terminal styrene radicals vs terminal methyl methacrylate radicals if it is assumed that the rate of crossover is constant:

$$\frac{[\mathrm{S}^{\bullet}]}{[\mathrm{MMA}^{\bullet}]} = \frac{r_{\mathrm{St}} k_{\mathrm{p,MMA}} [\mathrm{S}]}{r_{\mathrm{MMA}} k_{\mathrm{p,St}} [\mathrm{MMA}]} \tag{4}$$

in which $k_{\mathrm{p,St}}$ and $k_{\mathrm{p,MMA}}$ are the homopropagation rate coefficients for styrene and methyl methacrylate, respectively. The chance of a termination reaction occurring is directly related to the concentrations of the respective terminal radical endgroups. If it is assumed that a termination reaction between a styrene radical and a methyl methacrylate radical leads to termination by combination and that both termination by combination and termination by disproportionation occur at the same speed, then the overall chance of termination by combination occurring in the ultimate model can be expressed by

$$P_{\mathrm{comb}} = \frac{[\mathrm{S}^{\bullet}]^2 + 2[\mathrm{S}^{\bullet}][\mathrm{MMA}^{\bullet}]}{[\mathrm{S}^{\bullet}]^2 + 2[\mathrm{S}^{\bullet}][\mathrm{MMA}^{\bullet}] + [\mathrm{MMA}^{\bullet}]^2} = \left(1 + \frac{1}{\frac{[\mathrm{S}^{\bullet}]}{[\mathrm{MMA}^{\bullet}]}\left(\frac{[\mathrm{S}^{\bullet}]}{[\mathrm{MMA}^{\bullet}]} + 2\right)}\right)^{-1} \tag{5}$$

With $r_{\mathrm{St}} = 0.48$, $r_{\mathrm{MMA}} = 0.42$, $k_{\mathrm{p,St}} = 65$ L mol^{-1} s^{-1}, and $k_{\mathrm{p,MMA}} = 257$ L mol^{-1} s^{-1} and a feed composition of $f_{\mathrm{St}} = 0.053$, it can be estimated that $[\mathrm{S}^{\bullet}]/[\mathrm{MMA}^{\bullet}] \approx 0.25$, meaning that 36% of the termination reactions result in termination by combination (if the UM model is assumed to be valid). It is difficult to estimate this ratio from the isotopic pattern in Figure 1 for two reasons. First of all, the mass peaks that are the result of termination by disproportionation have been growing for approximately twice as long as the mass peaks that are the result of termination by combination and therefore may not be compared with each other. Second of all, there is an isotopic overlap between these mass peaks. Nevertheless, by a comparison of the peak areas of the two modes of termination in Figure 1, it can be estimated that approximately 60% of the peaks in this mass range are the result of termination by combination. The deviation between the estimated value and

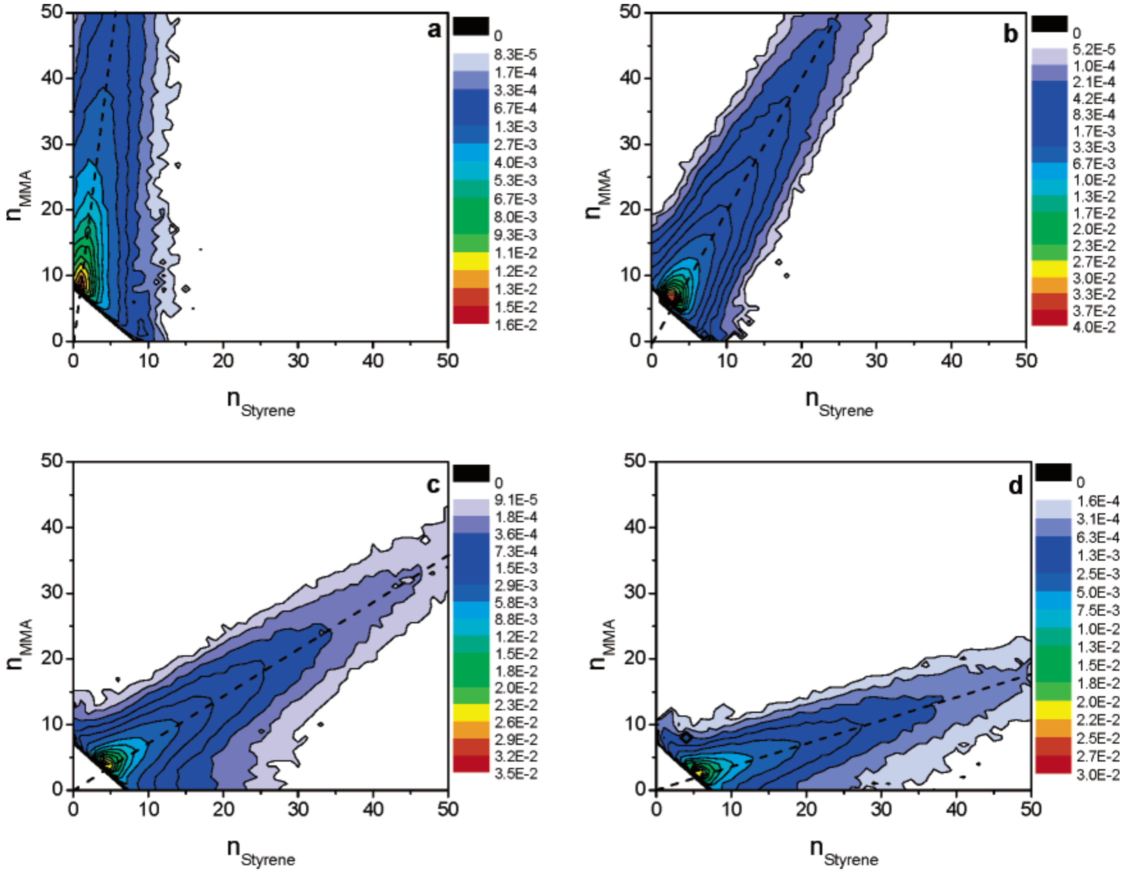

Figure 2. Copolymer fingerprints for PLP experiments carried out with methyl methacrylate and styrene at $f_{St} = 0.053$, frequency = 8 Hz (a), $f_{St} = 0.249$, frequency = 4 Hz (b), $f_{St} = 0.600$, frequency = 4 Hz (c), and $f_{St} = 0.792$, frequency = 4 Hz (d). The dashed lines in the copolymer fingerprint plots, which start out from the origin, are indicative of the average chemical composition of the copolymer.

the calculated value is primarily related to the different reaction time after the pulse (viz., differences in radical concentration) at which these polymer chains were created. However, within one experiment, because of the very low conversions (below 1%), no composition drift occurs, so the ratio of the two monomers and therefore the ratio of the two modes of termination remain constant within one experiment; this does not complicate the estimation of the ratio of modes of termination. Furthermore, the calculation of the ratio of terminal radicals is dependent on the model used to describe the copolymerization kinetics.[12] In the case of the penultimate model, predictions are that the ratio $[S^\bullet]/[MMA^\bullet]$ is even much higher, which is more in line with the results from MALDI-ToF-MS.

(3) From the isotopic distributions, it can be observed that chains which are the result of a termination by combination reaction consist predominantly of two benzoyl radicals (radical A), although there are also chains containing both a benzoyl endgroup and a benzyl alcohol endgroup (radical B).

Given the MALDI-ToF-MS spectrum at low styrene feed composition, it can be stated that, certainly at higher styrene feed compositions, most polymer chains are the result of termination by combination reactions. Combined with the fact that most chains terminated by combination have predominantly two benzoyl endgroups, this leads to the conclusion that the interpretation of the mass spectra can be simplified using only the combination of two benzoyl endgroups having a mass of 105.12 g mol^{-1}. At the low styrene feed compositions, this approach will lead to an error, but this error is estimated to be less than 2% at the higher chain lengths.[13] Together with the average masses of styrene ($M_{St} = 104.152$ g mol^{-1}) and methyl methacrylate ($M_{MMA} = 100.117$ g mol^{-1}) and the mass of the cation potassium ($M^+ = 39.10$ g mol^{-1}), these masses form the basis for the copolymer fingerprint analysis.[7]

In Figure 2, four examples are given for the copolymer fingerprints obtained by the analysis of four polystyrene-*co*-poly(methyl methacrylate) samples obtained by pulsed laser polymerization experiments at four different styrene feed compositions. These plots are the results of the copolymer fingerprint analysis[7] in which the copolymer is visualized as a two-dimensional matrix in which the axis corresponds to the number of styrene units (n_{St}) and methyl methacrylate units (n_{MMA}) present in the copolymer chain. The corresponding intensities of the mass spectrum are indicated by the different colors.

A very evident observation from the copolymer fingerprints is that an increase of the styrene feed composition also results in an increase of the styrene incorporation in the copolymer. The dashed lines in the copolymer fingerprints indicate that the average chemical composition is approximately constant and independent of the copolymer chain length.

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(13) To estimate this error, the MALDI-ToF-MS mass spectrum at low styrene feed composition was analyzed as if consisting of chains which are the result of solely termination by combination or of termination by disproportionation. The differences thus found in the chemical composition varied from 5% at low chain lengths to less than 2% at chain lengths larger than 50. The results of this procedure are located in the Supporting Information section

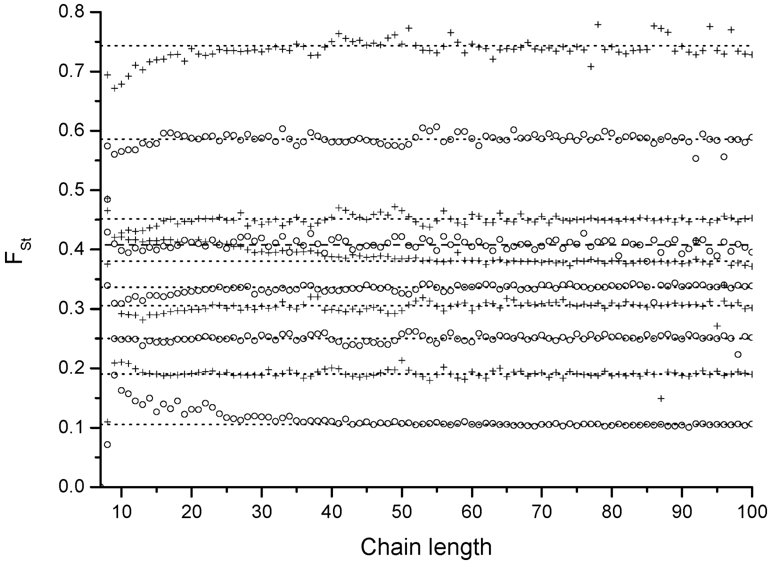

Figure 3. Average chemical composition of styrene, F_{St}, as a function of chain length for PLP experiments carried out at different styrene feed compositions. The average chemical compositions are directly evaluated from the copolymer fingerprints. The dotted lines indicate the long-chain limit of the average chemical composition evaluated between chain lengths 40 and 100.

MALDI-ToF-MS as a Tool for the Determination of Monomer Reactivity Ratios. The classical approach toward monomer reactivity ratio determination usually requires the determination of copolymer compositions, *F*, with, for example, ^{1}H NMR at low conversion experiments and relates these to the feed composition, *f*, by the instantaneous copolymerization equation:

$$F_i = \frac{r_i f_i^2 + f_i f_j}{r_i f_i^2 + 2 f_i f_j + r_j f_j^2} \tag{6}$$

There is one assumption for the use of this equation. It is known as the long-chain assumption which states that the monomer incorporated by initiation and transfer mechanisms is negligible compared to the monomer incorporated by propagation. When considering low conversion pulsed laser polymerization experiments, a whole range of polymer chains is created ranging from oligomers to very high molar masses. This implies that only that part of the molecular weight distribution can be used for the evaluation of the reactivity ratios in which the long-chain assumption is valid.

The copolymer fingerprints, of which a few examples have been shown in Figure 2, were used to evaluate the average chemical composition as a function of the chain length. This evaluation was carried out for all the duplicate experiments, although in Figure 3 only the results are shown for the PLP experiments carried out with higher laser energy. From Figure 3, two important observations can be made:

(1) The average copolymer chemical composition is constant for chain lengths of approximately 30 units or higher.

(2) The average copolymer chemical composition is chain-length dependent for chain lengths smaller than 30 units. The observed difference between copolymer composition and feed composition is largest for the smallest chain lengths and gradually decreases until the chemical composition reaches its long-chain limit.

The first observation is very important when compared to the results of Semchikov et al.[14] In Semchikov's work, it was observed that the chemical composition of polystyrene-*co*-poly(butyl acrylate) varies with the molecular weight of the copolymer, even up to very high masses. Semchikov et al. explained this behavior in terms of a preferential absorption model, in which one of the monomers preferentially absorbs in the growing polymer coil, thus creating its own locus of polymerization. Later on, Chambard et al.[15] disproved these observations for styrene−butyl acrylate, stating that the observations by Semchikov et al. were induced by their experimental procedures. The results of Figure 3 clearly agree with the results obtained by Chambard et al.[15] Also, these results are in line with the observation that the individual propagation rate coefficients are not chain-length dependent after say the addition of 10−20 monomer units.[4]

To understand the second observation, it is imperative to realize that the relationship between chain length and reaction time in a copolymerization reaction is not straightforward. In a pulsed laser polymerization experiment carried out for a homopolymer, at any moment in time, radicals which have originated from the same laser pulse are governed by a Poisson chain-length distribution. Because of this Poisson distribution, it can be assumed that there exists a clear relationship between chain length and time. With the introduction of a second monomer, this relationship between chain length and time becomes distorted. Chains richer in one monomer may propagate slower compared to chains richer in the other monomer because of differences in propagation and cross-propagation rates. These differences can result in radical chain-length distributions which may be characterized by a "broad" Gauss distribution where differences exist between the average chemical composition of radical chains at the lower chain lengths and radical chains at the higher chain lengths. With time proceeding after applying a laser pulse, these differences may become less important, but

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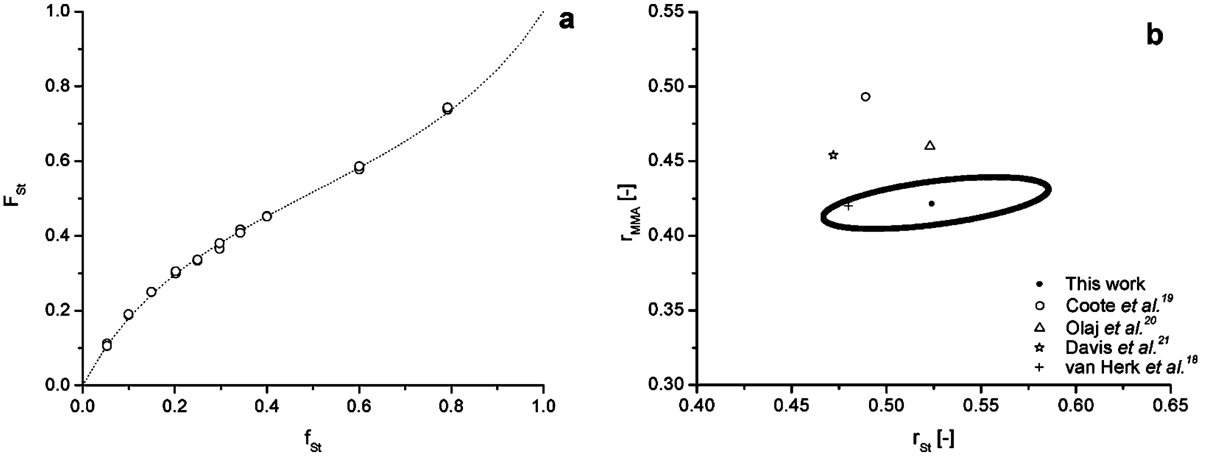

Figure 4. (a) Mayo−Lewis plot showing the correlation between the copolymer and feed composition for the copolymer system styrene and methyl methacrylate as determined by MALDI-ToF-MS. The dotted line refers to the best-fit using eq 4. (b) Best-fit value for the monomer reactivity ratio obtained by a least-squares analysis of the MALDI-ToF-MS data using an individual weighing scheme. Indicated is the 95% joint confidence interval constructed using the χ^2 distribution. The best-fit values thus obtained, $r_{St} = 0.523$, $r_{MMA} = 0.421$, are compared to several literature values from Table 2.

especially at the lower chain lengths, these differences can result in the deviations seen in Figure 3.

For the evaluation of the average chemical composition, only chain lengths between 40 and 100 units were used. Considering the use of MALDI-ToF-MS for the determination of reactivity ratios, there is one example in the literature where MALDI-ToF-MS has been applied for a kinetic analysis of the copolymer system methyl methacrylate and butyl methacrylate, created by catalytic chain transfer.[16] Although the authors were clearly able to measure the average chemical composition, they found a discrepancy between their MALDI-ToF-MS data and their composition data determined by ^{1}H NMR. As an explanation for this phenomenon, they postulated that this was due to the difference in hydrophobicity between the monomer units, thus resulting in discrimination effects due to ionization differences.

With respect to discrimination effects, MALDI-ToF-MS results always have to be interpreted with caution, even though we have previously shown two very successful examples where average chemical compositions determined by MALDI-ToF-MS and ^{1}H NMR were the same. The same holds true for the copolymer system styrene−methyl methacrylate. The advantage of this system is that it has been investigated extensively in the past, and therefore reliable estimates of monomer reactivity ratio data already exist in the literature, compiled by van Herk.[17] Simply comparing the results in this study with previously generated data should therefore be sufficient to judge whether mass discrimination effects due to ionization differences play an important role in this system. Comparing directly with ^{1}H NMR is problematic because of the low amounts of isolated polymer material, as all experiments are low conversion experiments. Moreover, the ^{1}H NMR would also take into account the contribution of low molecular weight material which, as shown in Figure 3, has a different chemical composition.

Table 2. Monomer Reactivity Ratio Parameters Taken from Literature and Obtained in This Work

	T (°C)	r_{St}	r_{MMA}
Coote et al.[19a]	20−60	0.489	0.493
Olaj et al.[20a]	25	0.523	0.46
Davis et al.[21a]	25	0.472	0.454
van Herk et al.[18a]	50	0.48	0.42
this work	15	0.523	0.421

[a] This value is the result of a combined data set of different literature values.

The monomer reactivity ratios were determined by fitting the copolymer composition data to eq 4; i.e., it is assumed that the IPUM is at work which seems to be a reasonable assumption when considering literature data compiled by van Herk.[17] To evaluate these monomer reactivity ratios, a nonlinear least-squares optimization was performed in which the weighing of the data was based on an individual error scheme. The 95% joint confidence interval was constructed using the χ^2 distribution. The individual errors were obtained by calculating the standard deviation of the average chemical composition between chain lengths 40 and 100. Figure 4a shows the Mayo−Lewis plot evaluated from the MALDI-ToF-MS data combined with the best-fit (dotted line) to eq 4 using the parameters from the nonlinear least-squares optimization. Figure 4b reveals the results of the nonlinear least-squares evaluation resulting in $r_{St} = 0.523$ and $r_{MMA} = 0.421$, combined with some monomer reactivity ratios from the literature. As can be observed from Figure 4b, the joint confidence interval is overlapping with the work of van Herk et al.[18] Furthermore, the obtained reactivity ratios are in close agreement with the other literature values as can be observed from both Figure 4b and Table 2, thus providing proof that mass discrimination due to ionization differences does not occur for the copolymer system styrene methyl−methacrylate.

Average Propogation Rate Coefficients (k_p^{avg}) by the PLP-MALDI-ToF-MS Method. In the literature, several examples exist where PLP-SEC has been used for the evaluation of homo- and copolymerization propagation rate coefficients (see Van Herk[17] for a compilation of literature values and Buback[17] for a description of the PLP-SEC method). The average propagation rate coefficients can subsequently be used to determine the reactivity ratio data and are as such a very powerful tool to study the copolymerization kinetics.

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(18) Herk, A. M. v.; Dröge, T. *Macromol. Theory Simul.* **1997**, *6*, 1263−1276.

To carry out these types of experiments, usually a range of monomer feed compositions are selected which are then subjected to pulsed laser polymerization experiments. Subsequently, a molecular weight distribution analysis is carried out by means of size exclusion chromatography.

The average propagation rate coefficient (k_p^{avg}) is then evaluated from the inflection point in the resulting molecular weight distribution, which is related to the average propagation rate coefficient according to

$$L_{0,i} = ik_p^{avg}[M]_{avg}t_p \qquad (7)$$

where $L_{0,i}$ is the characteristic chain length of the copolymer formed in the time between two laser pulses, t_p. $[M]_{avg}$ is the average monomer concentration, 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.

To measure the molecular weight distribution of the copolymer with SEC, several possible approaches exist. One suggestion by Davis et al.[21] implies a linear interpolation of the calibration curve for the copolymer by using the calibration curve for the homopolymers. This approach has been used quite frequently.[22−27] A better and more accurate option would be the use of Mark−Houwink relationships, which relate the average copolymer chemical composition to the hydrodynamic volume.[28,29] However, the determination of this relationship requires well-characterized copolymer standards which are not readily available. A third option and perhaps the best with regard to SEC would be the use of a triple-detector setup which in principle results in an absolute molar mass determination. Calibration of the triple-detector setup, however, is tedious and time consuming, but nevertheless, the method has been used to evaluate copolymer kinetics for several systems.[19,30−32]

In contrast to the aforementioned SEC method for measuring copolymer molecular weight distributions, MALDI-ToF-MS can be a very valuable tool as the method requires no additional actions to measure copolymer masses. Although the use of MALDI-ToF-MS has been suggested[30] in the literature for the analysis of average propagation rate coefficients, so far it has never been applied because the analytical method is usually underestimated in its capabilities of analyzing synthetic copolymers.

In a previous article on MMA and styrene homopolymerizations, we have shown that when working in the high termination rate limit, i.e., high initial radical concentrations, propagation rate coefficients have to be evaluated from the peak maximum in the number molecular weight distribution instead of the inflection point.[4]

In that same article, the combination of pulsed laser polymerization experiments and MALDI-ToF-MS analysis was used to investigate the chain-length-dependent propagation kinetics of the very first propagation steps. It was established that this chain-length-dependent behavior accumulatively may be observed until at least a chain length of 100 units, even though it is only limited to the first individual 10 propagation steps. To determine accurate average propagation rate coefficients for a copolymer system, the repetition rate of the laser therefore has to be chosen in such a way that the influence of the first 10 propagation steps can be safely neglected. Therefore, experiments have to be designed in such a way that the peak maximum is located at chain lengths above 100 units.

In Figure 5a−d, it can be observed that well-resolved spectra are obtained with clearly resolved first-order peak maxima. It can be clearly seen that these spectra contain individual peaks which can be attributed to the small mass difference between the monomer's styrene and methyl methacrylate. The evaluation of the average propagation rate coefficient is carried out by determination of the peak maxima. The results of this procedure are collected in Table 3 and visualized in Figure 6b, and as can be seen, all peak maxima are located well above a chain length of 100 units.

Radical Reactivity Rate Coefficients. The expression for the average propagation rate coefficient by the implicit penultimate unit model is given in eq 8 and can be used to obtain point estimates for the radical reactivity ratios, s_i and s_j.

$$k_p^{avg} = \frac{\bar{r}_i f_i^2 + 2 f_i f_j + \bar{r}_j f_j^2}{\dfrac{\bar{r}_i f_i}{\bar{k}_{ii}} + \dfrac{\bar{r}_j f_j}{\bar{k}_{jj}}} \quad \text{where} \quad \bar{k}_{ii} = k_{iii}\frac{r_i f_i + f_j}{r_i f_i + \dfrac{f_j}{s_i}} \qquad (8)$$

To obtain point estimates for the reactivity ratios, two different approaches can be undertaken: (i) the radical reactivity ratios can be determined independently from the (earlier) determined monomer reactivity ratios; and (ii) both monomer and radical reactivity ratios can be determined at once.

For both approaches, a nonlinear least-squares analysis was performed in which the weighing of the data was based on an individual error scheme. In the case of the four-parameter fit, the sum of squares is determined in a four-dimensional space. As a result of this, the joint confidence interval evaluated at the 95% confidence level will also represent a joint confidence interval in a four-dimensional space.

Note that the joint confidence intervals are the actual intervals and not the usual orthogonally approximated intervals often seen in the literature.[18] Visualization of this confidence interval may be obtained by projecting the four-dimensional confidence interval on a two-dimensional space, i.e., in this case, the radical reactivity ratios s_{St} and s_{MMA}. The results of the independent two-parameter fit and the four-parameter fit can be seen in Figure 6a together with the 95% confidence intervals. The obtained values are also collected in Table 4.

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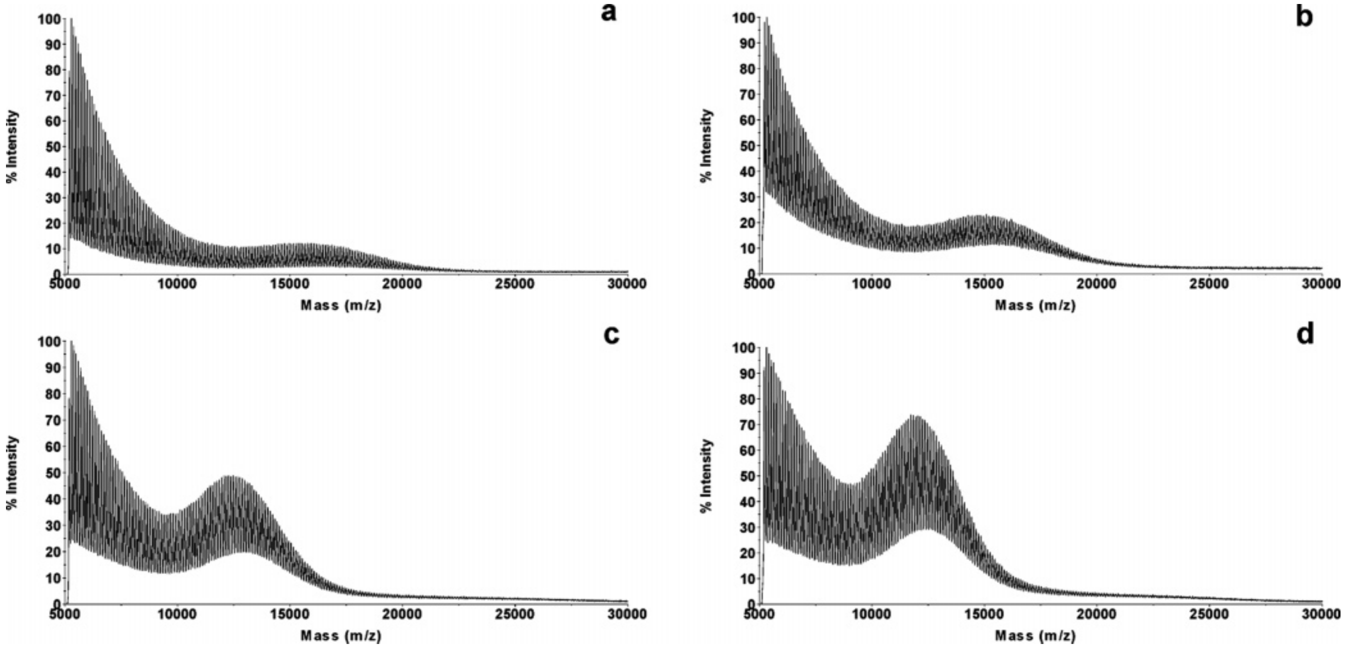

Figure 5. Examples for MALDI-ToF-MS mass spectra obtained by PLP experiments of the copolymer system styrene−methyl methacrylate. The spectra were analyzed in the linear mode at different styrene feed compositions. (a) $f_{St} = 0.053$, repetition rate = 8 Hz. (b) $f_{St} = 0.249$, repetition rate = 4 Hz. (c) $f_{St} = 0.600$, repetition rate = 4 Hz. (d) $f_{St} = 0.792$, repetition rate = 4 Hz.

Table 3. Indicated Are the Positions of the Peak Maxima in the MALDI-ToF-MS Spectra and the Average Propagation Rate Coefficient (k_p^{avg}) Obtained by Carrying Out Experiments at Different Feed Compositions and Laser Frequencies

f_{St} [-]	f [Hz]	$L_{0,1}$ [g mol^{-1}]	k_p^{avg} [L mol^{-1} s^{-1}]	$\Delta k_p^{avg\,a}$	f_{St} [-]	f [Hz]	$L_{0,1}$ [g mol^{-1}]	k_p^{avg} [L mol^{-1} s^{-1}]	$\Delta k_p^{avg\,a}$
0	12	201.17	257.46	6.40	0.297	4	159.11	69.27	2.18
0	12	200.17	256.18	6.40	0.297	4	159.11	69.27	2.18
0.053	8	156.14	133.71	4.28	0.342	4	150.13	65.57	2.18
0.053	8	159.14	136.27	4.28	0.342	4	150.13	65.57	2.18
0.100	6	166.10	107.01	3.22	0.400	4	141.10	61.87	2.19
0.100	6	166.10	107.01	3.22	0.400	4	141.10	61.87	2.19
0.149	5	163.11	87.87	2.69	0.600	4	122.15	54.32	2.22
0.149	5	164.11	88.41	2.69	0.600	4	121.16	53.88	2.22
0.202	5	149.14	80.64	2.70	0.792	4	117.23	52.85	2.25
0.202	5	147.14	79.56	2.70	0.792	4	116.23	52.40	2.25
0.249	4	171.08	74.24	2.17	1	4	141.87	64.93	2.29
0.249	4	171.08	74.24	2.17	1	4	140.88	64.47	2.29

[a] The absolute errors in the average propagation rate coefficient (k_p^{avg}) were evaluated by transposing the error in the location of the peak maximum in the k_p^{avg} by the following equation: $\Delta k_p^{avg} = \Delta L_{0,1} \cdot f/[M]_{avg}$. To evaluate the error in k_p^{avg}, it was assumed that the peak maximum could be determined with an accuracy of 5 repeat units, e.g., $\Delta L_{0,1} = 5$.

The most important observation that can be inferred from Figure 6a is related to the size of the joint confidence intervals. The coupled determination of the reactivity ratios leads to an increase of the joint confidence interval with respect to the radical reactivity ratios, whereas the confidence intervals for the monomer reactivity ratios are virtually the same.[33] The reason for this is directly related to the size of the sum of squares for the two different data sets. From Table 4, it can be observed that the value for the sum of squares for the monomer reactivity ratios is the largest and therefore is responsible for the largest part of the total sum of squares. Because the joint confidence intervals are closed in all directions, both parameters are statistically determined. Often s_{MMA} is undetermined because of the low accuracy of the data.

If Figure 6b is considered, then the independent data fit, as well as the coupled data fit, lead to a virtually indistinguishable fit for the average propagation rate data. It is only from Table 4 that it can be observed that the four-parameter fit will lead to a smaller total sum of squares and is therefore preferred over the independent 2 × 2 parameter fit.

Copolymer Chemical Composition Distribution. MALDI-ToF-MS combines the unique ability that within one simple measurement both a molecular weight distribution and a chemical composition distribution can be obtained. Because the pulsed laser polymerization experiments were carried out at low conversions, therefore excluding composition drift, the measured chemical composition distributions can be directly compared to the Stockmayer equation.[34] The Stockmayer equation can however only be applied in the long-chain limit and is therefore incapable of describing the variation of the chemical composition distribution at the lower chain lengths. For this reason, refuge was taken in the use of the Monte Carlo simulation. For a detailed description of the procedure used, see ref 11.

The advantage of the Monte Carlo simulation is that the complete pulsed laser polymerization reaction can be simulated,

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(33) The comparison between the 95% joint confidence intervals, obtained by the coupled four-parameter fit and Figure 6a, can be found in the Supporting Information section.

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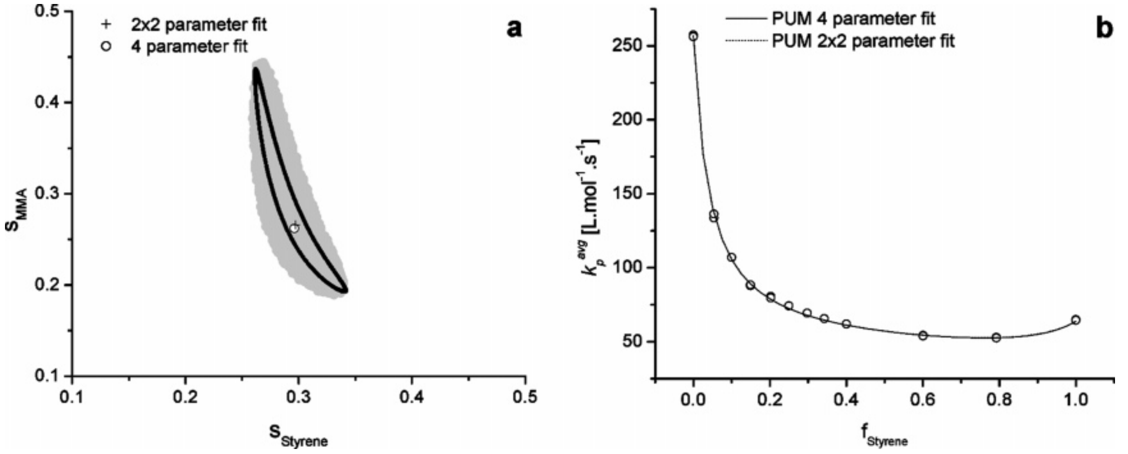

Figure 6. (a) Joint confidence intervals (95%) evaluated using a χ^2 analysis in which the weighing of the data is performed using an individual weighing scheme. The two-parameter fit results in a "normal" contour plot (black line) with best-fit values $s_{St} = 0.297$ and $s_{MMA} = 0.266$. The four-parameter fit results in a gray projection of the least-squares analyses with best-fit values $s_{St} = 0.296$ and $s_{MMA} = 0.262$. (b) Average propagation rate coefficient (k_p^{avg}) as determined by MALDI-ToF-MS. Indicated are datapoints (○) together with the best-fit by the implicit penultimate unit model (eq 5) using the reactivity ratios as determined by the four-parameter fit (solid line) and the two-parameter fit (dashed line).

Table 4. Best-Fit Values for the (Independent) 2 × 2 Parameter Fit and the Coupled Four-Parameter Fit[a]

	monomer reactivity ratios					radical reactivity ratios					
	r_{St}±		r_{MMA}±		ss	s_{St}±		s_{MMA}±		ss	ss_{tot}
2 × 2 parameter fit	0.523	−0.057 +0.063	0.421	−0.016 +0.018	13.99	0.297	−0.035 +0.045	0.266	−0.074 +0.170	3.68	17.67
4-parameter fit	0.517	−0.052 +0.058	0.420	−0.017 +0.017	14.08	0.296	−0.036 +0.044	0.262	−0.073 +0.182	3.49	17.57

[a] Also indicated are the sum of squares (ss) values for the monomer reactivity ratios and the radical reactivity ratios together with the total sum of squares.

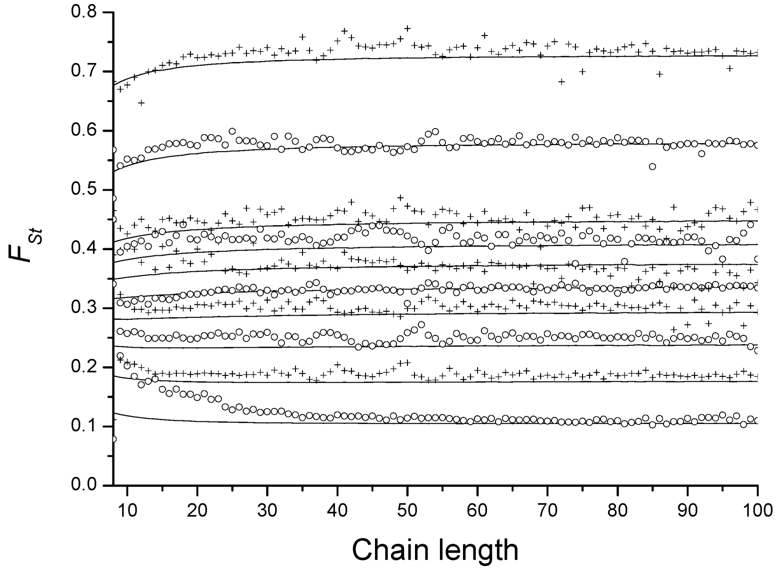

Figure 7. Average chemical composition of styrene, F_{St}, as a function of chain length as measured by MALDI-ToF-MS (symbols) compared to the results of Monte Carlo simulations (solid line). Input for the Monte Carlo simulation: $k_{p,St} = 64.7$ L mol^{-1} s^{-1}, $k_{p,MMA} = 256.8$ L mol^{-1} s^{-1}, $k_{t(i,j)} = 1 \times 10^8 (ij)^{-(0.2)/2}$ L mol^{-1} s^{-1}, $[M]_{tot} = 10$ mol L^{-1}, $[R]_0 = 1 \times 10^{-6}$ mol L^{-1}, $r_{St} = 0.523$, $r_{MMA} = 0.421$, $s_{St} = 0.297$, $s_{MMA} = 0.266$. Experimental simulation conditions are given in Table 3.

including the resulting microstructure of the copolymer. This allows for a detailed investigation into the dependence of the average chemical composition as a function of the chain length. As was stated earlier, in the lower chain-length regions, the difference between the copolymer composition and feed composition is the largest for the smallest chain lengths. The question was raised whether this behavior could be described by Monte Carlo simulations. The results of this Monte Carlo simulation are included in Figure 7. Simulations were carried out with the experimental conditions in Table 3 and the reactivity ratios determined in this article. If the results of this simulation are compared to the measurements carried out with MALDI-ToF-MS, it can be observed that the simulation results in the same trend as that of the MALDI-ToF-MS analysis. That there is still some difference between experiment and simulation may partly be ascribed to the fact that the Monte Carlo simulation does not take copolymerization termination into account. Instead, the simulation uses one simple power law to evaluate the chain-

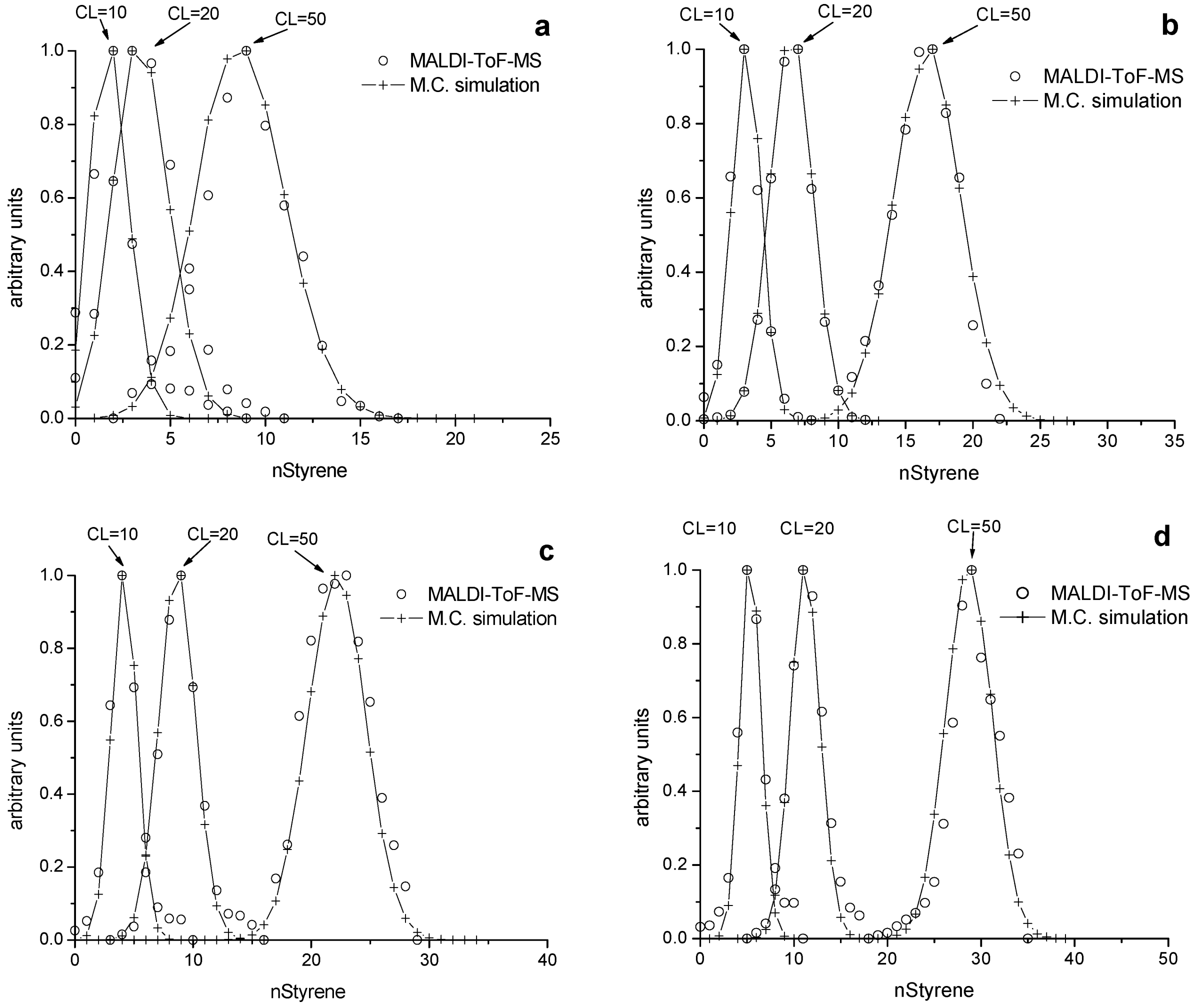

Figure 8. Comparison of the copolymer chemical composition distributions as obtained by the MALDI-ToF-MS copolymer analysis (○) and the Monte Carlo simulation (− + −) evaluated at three different polymer chain lengths. The comparison was carried out for four different feed compositions: $f_{St} = 0.100$ (a), $f_{St} = 0.249$ (b), $f_{St} = 0.400$ (c), $f_{St} = 0.600$ (d).

length-dependent termination rate of a radical, regardless of its chemical composition or terminal radical. Moreover, it is assumed that only termination by combination takes place.

The copolymer chemical composition distribution was also compared to the Monte Carlo simulations for four different feed compositions at three different chain lengths. The results of this comparison can be observed in Figure 8 from which it may be concluded that there is a very good agreement between the MALDI-ToF-MS analysis and the Monte Carlo simulation.

Conclusions

Pulsed laser polymerization experiments were performed for the copolymerization system methyl methacrylate−styrene and analyzed by MALDI-ToF-MS. MALDI-ToF-MS was used to determine chemical composition distributions of the resulting copolymers, as well as the determination of average propagation rate coefficients, information on the mode of termination, and chain-length dependency effects. The average chemical compositions of the resulting copolymers were fitted to the Mayo−Lewis plot and resulted in point estimates of the monomer reactivity ratios which are in line with data found in the literature. Furthermore, the average propagation rate data were fitted to the implicit penultimate unit model and resulted in new point estimates of the radical reactivity ratios. Finally, the results of this analysis were compared to the results of a Monte Carlo simulation, confirming the successful analysis of copolymer mass spectra by MALDI-ToF-MS.

The results described in this paper are believed to have resulted in the most complete and accurate parameter set in copolymerization studies to date. As the proposed analysis method can result in detailed information on copolymerization kinetics as well as the chemical composition distribution, the mode of termination, and chain-length dependency effects, it can be regarded as a very valuable tool for further future kinetic studies.

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Supporting Information Available: Both an error estimation of the MALDI-ToF-MS analysis for determination of the average chemical composition and a comparison between the 95% joint confidence intervals, obtained by the coupled four-parameter fit and Figure 6a. This material is available free of charge via the Internet at http://pubs.acs.org.

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