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Pulsed-Laser Polymerization/Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry: An Approach toward Free-Radical Propagation Rate Coefficients of Ultimate Accuracy?

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ABSTRACT: Free-radical polymerizations of styrene (S) and methyl methacrylate (MMA) in bulk were induced at 25 and 60 °C using a pulsed ultraviolet excimer laser. Molecular weight distributions (MWDs) of the polymer products produced were measured by both size exclusion chromatography and matrix-assisted laser desorption/ionization mass spectrometry and compared with one another. Propagation rate coefficients k_p were determined from these MWDs taking into account impacts of varying termination rates and varying pulse periods as well as errors resulting from instrumental broadening. Values of k_p(25 °C, S) = 96.5 L mol^{-1} s^{-1}, k_p(60 °C, S) = 364 L mol^{-1} s^{-1}, k_p(25 °C, MMA) = 372 L mol^{-1} s^{-1}, and k_p(60 °C, MMA) = 962 L mol^{-1} s^{-1} are finally suggested.

Introduction

Pulsed-laser polymerization (PLP) together with the determination of the molecular weight distribution (MWD) of the resultant polymer product by size exclusion chromatography (SEC)—the method almost always used for this purpose to date—has now been widely accepted as being a key free-radical polymerization kinetics experiment[1−3] because it permits values of propagation rate coefficients k_p to be measured very accurately, i.e., virtually free of assumptions. Despite this unique feature, the approach—which so far might most conveniently have been referred to as the PLP/SEC method—has up to now been hampered by some limitations inherent to SEC. These include the need for molecular weight (MW) calibration[4] (this being generally difficult with respect to measuring MWDs of other than linear homopolymers, as, for instance, branched polymers and/or copolymers, mainly because of the lack of suitable calibration standards) and the occurrence of considerable instrumental broadening of the experimental MWDs.[3,5]

This paper focuses on experiments in which the MWD measurement part of the PLP technique—which hereafter will more generally be referred to as the PLP/MWD method—has been performed by both SEC and MALDI-MS (matrix-assisted laser desorption/ionization mass spectrometry). SEC and MALDI-MS results for k_p will be compared with respect to the accuracy of the MW scale (as was recently done for the first time by Danis et al.[4]) and in particular with respect to MW errors resulting from broadening of the experimental MWDs. The title notion that MALDI-MS might be the ultimate choice for determining accurate k_p values from PLP/MWD data relates to the combination of facts that measuring accurate MWDs is the most crucial part of the PLP/MWD technique and that MALDI-MS (or some subsequent, as yet unknown, even better future variant of high MW mass spectrometry) is regarded as the ultimate means of accurate and precise measurement of MWs.

PLP/MWD Method

The concept of obtaining the propagation rate coefficient k_p for radically polymerizable monomers of concentration c_M by a pulse-initiated polymerization followed by a determination of the MWD of the polymer produced has repeatedly been outlined during recent years (see, for instance, refs 1−3 and 5 as well as references cited therein). The method basically says that, according to

$$k_p = i_{\Delta T}/(c_M \Delta T) \qquad (1)$$

k_p may directly be read from structured MWDs resulting from PLP, if the chain length $i_{\Delta T}$, which corresponds to polymer molecules that have grown over an integer multiple of the time interval ΔT between successive laser pulses, is identified with characteristic inflection points or maxima of peaks within these MWDs.

The application of the technique spread rapidly only after Olaj et al.[6] suggested its use as a tool of "direct determination of the rate constant of chain propagation" in 1987. The first proposal for determining k_p "from the data of the position of the peak" within MWDs of polymer material obtained from "polymerization by periodic pulse initiation", however, stems from Genkin and Sokolov.[7] These and other authors studied the kinetics of pulsed-laser-initiated polymerization in detail 1 decade earlier.[7,8]

Experimental Section

Pulsed-laser polymerizations were performed with styrene (S) and methyl methacrylate (MMA) in bulk. Monomer concentrations of S of 8.651 and 8.344 mol L^{-1} as well as of MMA of 9.269 and 8.909 mol L^{-1} to be used within eq 1 at 25

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and 60 °C, respectively, were taken from the literature.[9] MWDs of the resulting polymer material were measured by means of SEC and MALDI-MS.

Pulsed-Laser Polymerizations. Monomers were destabilized by washing with dilute alkali and subsequently passed through a column filled with activated alumina (aluminum oxide 90; Merck). 2,2-Dimethoxy-2-phenylacetophenone (DMPA; Aldrich) was used as the photoinitiator in concentrations of around 5 mmol L^{-1} as received. A pulsed ultraviolet (UV) excimer laser (RD-EXC-150; Radiant Dyes Lasers & Accessories) was operated at a wavelength of 308 nm (XeCl) and optionally used together with a dye laser (Radiant Dyes Lasers & Accessories) to produce UV light pulses at a wavelength of 355 nm. Pulse widths were ca. 20 ns.

The reactions were carried out in quartz tubes which, after purging with He, were sealed with quartz windows. The quartz tubes were thermostated at the desired temperature of 25 or 60 °C to within ±0.2 °C. Directly after laser irradiation, the monomer samples were diluted with excess dichloromethane (Lichrosolv; Merck), which contained a small amount of 2,2,6,6-tetramethylpiperidine-1-oxyl free radical (TEMPO; Janssen Chimica) as inhibitor.

Laser pulses were either directed into the reaction volume at the maximum energy level possible or optionally attenuated to roughly 1% using suitable glass filters (type NG12 for 308 nm; Schott). Care was taken to ensure homogeneous illumination of the reaction volume. Absorptions of the reaction mixtures at the respective laser wavelength were controlled by UV spectroscopy to be ≤ 0.5 for monomer layers of about 1 cm thickness prior to laser exposure. The actual energy per area of illuminated monomer surface (EPAIMS) was measured through suitable apertures by averaging over 100 single pulses using a pyrometric energy detector (PRJ-M; Gentec). At 308 nm the maximum and attenuated EPAIMS were about 150 and 2 mJ cm^{-2}, respectively. At a wavelength of 355 nm (at which, compared to 308 nm, photons are less rich in energy by about 13%), only relatively low "maximum EPAIMS" of around 4 mJ cm^{-2} were available which were therefore *not* attenuated further. For further experimental details, see, e.g., ref 3.

Size Exclusion Chromatography. When the MWDs of the polymers formed during PLP were analyzed by means of SEC, the monomer conversions were simultaneously controlled via calibrated differential refractometer (RI 71; Merck) signals to ensure that they were always below 1%. Five columns (Ultrastyragel, 500, 10^3, 10^4, 10^5, and 10^6 Å; Waters) were used at 25 °C. The eluent was dichloromethane (Lichrosolv; Merck) with a flow rate of 1 mL min^{-1}. Calibrations were performed with polystyrene (PS) or poly(methyl methacrylate) (PMMA) standards, which had narrow MWDs and precisely known MWs (Polymer Standards Service).

Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry. MALDI-MS measurements of MWDs were performed on a Bruker Reflex II ® time-of-flight (TOF) mass spectrometer. The instrument operates with a LSI nitrogen laser providing 3 ns pulses of up to about 250 μJ at 337 nm. The laser beam is focused onto a sample area of about 50 μm × 100 μm resulting in power densities of 1−10 MW cm^{-2}. The desorbed ions are accelerated up to 35 keV and may be detected either in the reflectron or in the linear mode. While the reflectron mode allows for superior mass resolution, it is restricted to relatively low MWs of, say, 10^4 g mol^{-1} and frequently gives distorted results with respect to the true shape of an MWD. The linear mode of the detector gives more reliable results with respect to the true shape of an MWD of a polymer sample and at the same time permits the measurement of MWs of, say, 10^5 g mol^{-1} and above. Compared with the reflectron mode, the MW resolution capability is, however, considerably reduced. In the linear mode the detector consists of a dynode followed by a microchannel plate. Following the microchannel plate there is a scintillator and a photomultiplier for the detection of MWDs of polymers. All measurements reported in the present paper were recorded in the linear mode.

Samples were prepared from 10 μL of 10^{-4} mol L^{-1} solutions of polymer in tetrahydrofuran (THF), each of which was added to 10 μL of a 0.1 mol L^{-1} THF solution of the matrix 1,8,9-trihydroxyanthracene (Aldrich, Steinheim) or indolic acrylic acid (Aldrich, Steinheim) for measurements of PS or PMMA, respectively. For the detection of positive ions, 1 μL of a 5 g L^{-1} THF solution of silver trifluoroacetate (Aldrich, Steinheim) was added to the polymer/matrix/THF solution; 1 μL of the final mixture was applied to the multistage target of the mass spectrometer and air-dried. Single primary mass spectra were recorded from accelerated ions desorbing from the solid sample as a result of single-nitrogen-laser shots on it. Final mass spectra were obtained as averages over 100 single-laser-shot experiments, smoothed with a 10−20 point triangular weighting function, and base-line corrected. Prior to measurement, a PS standard of a peak MW of about 6000 g mol^{-1} (Polymer Standards Service) was used for external mass calibration.

Results and Discussion

SEC/MALDI-MS Comparison Using Mixtures of Molecular Weight Standards. MALDI is a "soft" ionization technique for transferring large molecular ions such as proteins or synthetic polymers into a mass spectrometer without fragmentation. The term "matrix-assisted" was used by Hillenkamp and co-workers (see, for instance, ref 10) when they reported the use of *inter alia* nicotinic acid as a matrix compound to permit laser desorption of peptides. The applications of MALDI-MS have expanded very rapidly so that it has already become a substantial subfield in mass spectrometry. However, up to now only a limited number of applications of MALDI-MS for the determination of MWDs of synthetic polymers has been described (see, for instance, refs 4 and 11−14). Only two recently published papers deal with the reliability and the exactness of the derived MWD data.[13,14]

There is no question that the accuracy of mass spectrometry in comparison to SEC is very much higher when MWs of single molecular species are measured at MWs of, say, below 10 000 g mol^{-1}. On the other hand, with respect to the intensity of individual mass signals relative to one another within the course of a whole distribution of MWs of a polymeric sample, MALDI-MS frequently gives distorted results. Up to now, for instance, low MW species frequently appear more intense relative to higher MW species.[12] It is for this reason that we will first compare SEC and MALDI-MS results for polymer samples of *known* MWDs.

Figure 1a shows MWDs obtained for a mixture of three low-polydispersity MW standards of PS in weight fractions of 1:1:1 by means of SEC (full curve) and MALDI-MS (dotted curve). At first glance the agreement of MWD results of SEC and MALDI-MS with one another may be said right away to be excellent. It is estimated that this is all the more so as a closer look at the MWDs in Figure 1a reveals that the *nominal* peak MWs of the standards of 9130, 19 600, and 34 300 g mol^{-1} (which are indicated as broken vertical lines) and the *experimental* peak MWs (both within SEC and MALDI-MS signals) are obviously not quite identical. Referring to the SEC signal, this finding apparently indicates an error in the calibration procedure, since it is the nominal peak MW of the standards which enters into the calibration of MWs to chromatographic elution volumes. However, within the present study, MW calibration within SEC was performed not only from the MWDs shown in Figure 1a but also from a total of 12 MW standards with peak MWs spreading from around 10^3 to 10^6 g mol^{-1}. Fitting a calibration function to all of the resulting pairs of MW/elution volume data is likely to result in a compensation of peak MW errors of

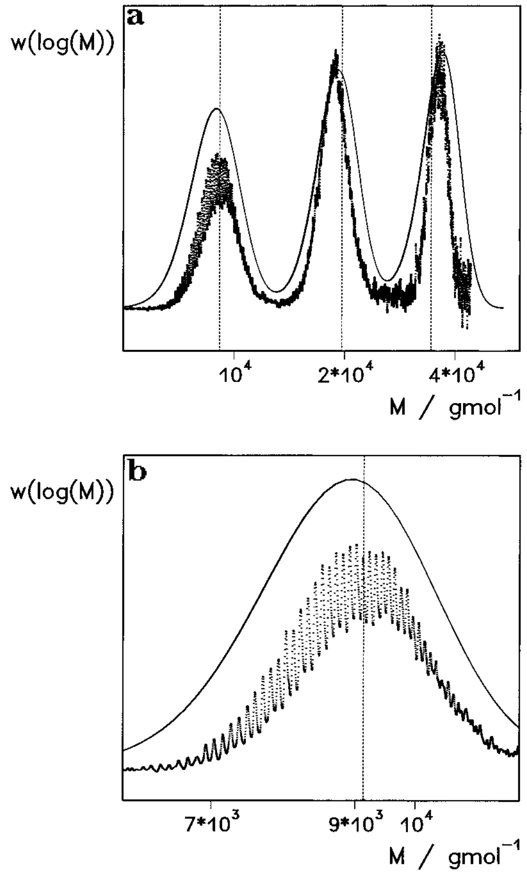

Figure 1. (a) Comparison of MWD results obtained for a mixture of three low-polydispersity molecular weight standards of PS in weight fractions of 1:1:1 by means of SEC (full curve) and MALDI-MS (dotted curve). Ordinate values of $w(\log(M))$ are given in arbitrary units. Nominal peak molecular weights of the standards of 9130, 19 600, and 34 300 g mol^{-1} given by the supplier are indicated as broken vertical lines. (b) Low molecular weight part of Figure 1a replotted on an expanded molecular weight scale.

inidividual standards to some extent. Thus the close agreement of SEC and MALDI-MS results in Figure 1a appears even more convincing in that the *MALDI-MS result obviously compares better to the "corrected" SEC result than to the nominal MWs* of investigated standards. The observed agreement of MWDs in Figure 1a is even more worthwhile mentioning in view of the considerable experimental effort necessary for reliable and precise characterization of absolute MWs of MW calibration standards and in view of the fact that almost identical absolute MWs are obtained by two different, completely independent analytical tools.

The ratio of signal to noise (S/N) is obviously much better in the SEC signal. Because MWDs are generally obtained as *number distributions* in MALDI-MS, a change to lower S/Ns is to be expected in the high MW region of $w(\log(M))$ representations of these MWDs. At first sight, the S/N within the MALDI-MS signal of Figure 1a appears to be the best for the intermediate MW peak. However, within the low MW peak, the MALDI-MS signal already starts to be resolved into signals from single MW species and looks like a poor S/N only because of the chosen MW scale in Figure 1a. This is obvious from Figure 1b, where the low MW part of Figure 1a is replotted on an expanded MW scale. Downward from MWs of around 2×10^4 g mol^{-1}, the noise, i.e., the *statistical fluctuations* of the MALDI-MS signal, is increasingly transformed into a *regular form of fluctuations*, i.e., into signals of single-chain molecules. The spacing of the peaks corresponds exactly to the MW of the monomer S. Only one homologous series of PS chains is to be observed in Figure 1b. This may be taken as an indication that the standard was produced under very-well-controlled conditions. Actually it was made via anionic polymerization started by butyllithium. Because of its power of resolving MWDs into peaks of MW individuals, MALDI-MS appears to be predestined for the measurement of certain end groups of polymer chains and as such opens up very interesting perspectives for the detailed study of, e.g., different termination mechanisms in free-radical polymerization. Such concern—which up to now seems to be restricted to MWs of, say, around 10^4 g mol^{-1} or below—is beyond the scope of the present paper, however.

By integrating the SEC signal of Figure 1a, weight fractions of 1:1:1 for the relative amounts of the three MW standards are regained to within about 1% if the minima in between the three peaks are used as integration limits. Using the same procedure for the MALDI-MS signal, weight fractions of roughly 1:1.5:1.1 are obtained, where 1, 1.5, and 1.1 correspond to the amounts of the standards of the lower, the intermediate, and the higher MW, respectively. The fact that MALDI-MS up to now has difficulty in reliably detecting the relative amounts of polymer within the course of an MWD has been mentioned above. The appearance of this phenomenon is known to be *particularly significant for broader MWDs* with polydispersities of, say, 1.1 and above.[13,14] Most frequently MALDI-MS typical distortions of MWDs result from the tendency to *underestimate* the amounts of higher MW species relative to amounts of lower MW species and from the occurrence of dimer (as well as trimer and higher *n*-mer) signals of a given MW peak. The intensity of such *n*-mer signals is *inter alia* dependent on the laser energy used for ionization during the MALDI process and on the polymer/matrix mass ratio and may correspondingly be controlled within certain limits. From the observation that the relative amounts of polymer detected within the MALDI-MS and the SEC signal in Figure 1a over an extended MW range from well below 10^4 up to nearly 10^5 g mol^{-1}, as well as from the observation that the symmetries of MALDI-MS and SEC signals obtained for individual MW standards compare, if not perfectly, then at least favorably with one another, we may assume that the distortion of the MALDI-MS signals within such *narrow* MWDs as, for instance, those of individual standards shown in Figure 1a is comparatively small—if not negligible. Such MWDs would generally not allow for interference from dimers or higher *n*-mers of any MW individual contained in them.[15] The similarity of the shapes of MALDI-MS and SEC signals is even more clearly evident from Figure 1b if one looks at the envelope of the MALDI-MS signal. Because the peak symmetry is more or less identical for both signals, while the peak MWs compare very favorably with one another, there is correspondingly little room for over- or underestimation of the low and high MW tails of the peaks, respectively, that is, for an erroneous estimation of the relative amounts of polymer chains of different lengths. Dimers of individual chain molecules of MW of, say, 7000 g mol^{-1} occurring in relatively low abundance at the low MW end would already occur roughly at the high MW end of the MWD in Figure 1b, while no (singly charged) trimer or higher *n*-mer of any individual chain molecule with significant abundance could ever occur within the MW range of the distribution shown here.

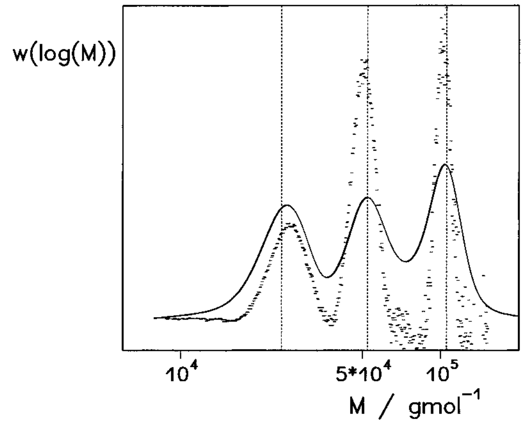

Figure 2. Comparison of MWD results obtained for a mixture of three low-polydispersity molecular weight standards of PMMA in weight fractions of 1:1:1 by means of SEC (full curve) and MALDI-MS (dotted curve). Ordinate values of $w(\log(M))$ are given in arbitrary units. Nominal peak molecular weights of the standards of 24 400, 52 200, and 105 000 g mol^{-1} given by the supplier are indicated as broken vertical lines.

According to Figure 1a, the widths of the MWDs of single standards appear significantly narrower in the MALDI-MS signals as compared to the SEC signals. Given the above, the reason for this observation is clearly a result of the very much lower MW-resolving power of SEC in comparison to MALDI-MS (compare Figure 1b) or, in other words, of the considerable instrumental broadening which is generally inevitable in size exclusion chromatographic investigations, particularly of comparatively narrow MWDs. However, the MALDI-MS signal is also not completely free of broadening, the extent of which may actually be estimated from the widths of individual peaks in Figure 1b, which should theoretically be almost infinitely sharp.

Figure 2 shows $w(\log(M))$ representations of MWDs obtained for a mixture of three low-polydispersity MW standards of PMMA in weight fractions of 1:1:1 by means of SEC (full curve) and MALDI-MS (dotted curve). The nominal peak MWs of the standards of 24 400, 52 200, and 105 000 g mol^{-1} given by the supplier are indicated as broken vertical lines.

With respect to absolute MWs, the agreement between SEC and MALDI-MS results is again convincing. While the S/N of the MALDI-MS signal is by no means as good as that of the SEC signal, the latter shows significantly broader distributions, a difference which is attributed, as above, to the much higher mass resolution power of MALDI-MS compared to SEC. Because the calibration mixture contained no standard of sufficiently low MW as to allow for a single-chain resolution to be achieved, the decrease in S/N with MW (which was partly masked in Figure 1a) is clearly evident in Figure 2.

The calculation (by integration) of the weight fractions of the three PMMA standards in the calibration mixture used is uncertain for the SEC signal in Figure 2 because of considerable peak overlap. It may however be expected that the ratio of weight fractions of the lower, the intermediate, and the higher MW standard is not very much different from 1:1:1. From the MALDI-MS signal in Figure 2, such a ratio of ca. 1:1.7:0.9 was obtained by integration. The same inferences which were made with respect to the relative weight fractions obtained from the MALDI-MS signal in Figure 1a should apply here.

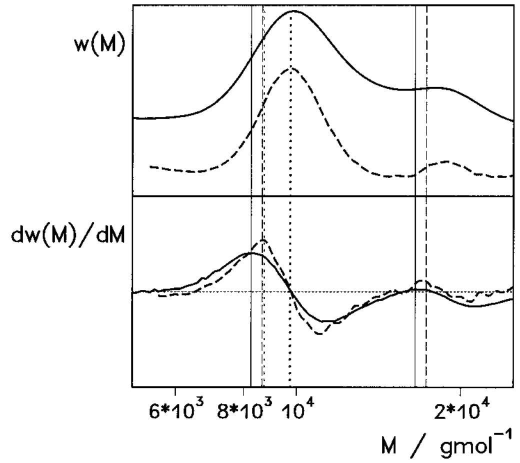

Figure 3. Experimental distributions $w(M)$ as obtained by means of SEC (full lines) or MALDI-MS (broken lines) together with numerically obtained derivatives $dw(M)/dM$ thereof for a PLP of bulk S at 25 °C using laser pulses of an EPAIMS of 6 mJ cm^{-2} at 355 nm with a period of $\Delta T = 0.1$ s. Values of ordinates were plotted in arbitrary units against molecular weight M. Values of molecular weights at the LMWSIPs of these MWDs and 2-fold multiples thereof have been indicated as full and broken vertical lines for SEC and MALDI-MS curves, respectively. Values of molecular weights at the maximum and at the approximate theoretical LMWSIP of the dominating PIO peak are indicated as dotted bold and fine vertical lines, respectively. A value of $dw(M)/dM = 0$ is indicated as a horizontal dotted line.

We may summarize by saying that MALDI-MS methods are available for PS and PMMA which permit accurate absolute MW determinations, particularly of narrow MWD structures comparable to those of Figures 1 and 2 up to MWs of at least, say, 10^5 g mol^{-1}. The ability to measure reliably such narrow MWD structures is a predominant requirement for applications of the PLP/MWD technique with respect to accurate k_p values. The fact that we are still unable to estimate with complete reliability the relative amounts of polymer in the course of *broad* MWDs seems to be of no concern when one is restricted to such *narrow* MWDs. Moreover, much of the instrumental broadening problem seems to be avoided when one uses MALDI-MS instead of SEC.[3,5]

SEC/MALDI-MS Comparison of PLP/MWD Results for the Styrene k_p. Figure 3 shows weight representations $w(M)$ of MWDs obtained by means of SEC (full line) and MALDI-MS (broken line) together with corresponding derivatives $dw(M)/dM$ with respect to MW M for PS produced by PLP at 25 °C using pulses of a maximum available EPAIMS of 6 mJ cm^{-2} at 355 nm with a period of $\Delta T = 0.1$ s, i.e., with a pulse frequency of 10 Hz. The MWDs contain a first and dominant pulsed-initiation-originating (PIO) peak at around 10^4 g mol^{-1} and a significantly smaller one at around 2×10^4 g mol^{-1}. Compared with the SEC result, the relative weight fraction of polymer in the region of the second, i.e., higher, MW PIO peak within the MALDI-MS curve appears to be considerably lower.

Values of MWs $M_{\Delta T}$ at the low MW side inflection points (LMWSIPs) of these MWDs and 2-fold multiples thereof have been indicated as full and broken vertical lines for SEC and MALDI-MS curves, respectively. Inflection points were determined as maxima of numerically obtained derivatives $dw(M)/dM$. In the case of the MALDI-MS signal, this procedure could only be applied after the peaks resulting from resolution into single-MW individuals were smoothed out from the lower MW PIO peak mathematically.

While it was originally proposed by Olaj et al.[6] to determine $i_{\Delta T}$ and as such k_p (cf. eq 1) from LMWSIPs within *number* MWDs of PIO polymer, it was recently suggested that the best easy available (i.e., without the need for, e.g., complicated modeling available) measure of $i_{\Delta T}$ should be the maximum or the LMWSIPs within *weight* MWDs[3,5] depending on whether sufficiently high or low concentrations of radicals were being produced per initiating pulse during PLP. The former and the latter limiting experimental situations of the PLP technique were referred to as the high- and low-termination rate limits, respectively.[3,5] Because it has so far been common practice, and also because it appears up to now to be difficult to decide *a priori* whether one is definitely working in the high- or low-termination rate limit, we might start with the assumption that the MWs $M_{\Delta T}$ taken from the LMWSIPs indicated in Figure 3 *were* the best measures of the chain length $i_{\Delta T}$. Using the MW of monomeric S of $M_M = 104.15$ g mol^{-1} in

$$i_{\Delta T} = M_{\Delta T}/M_M \tag{2}$$

k_p(S, 25 °C) was thus determined from eq 1 as 91.5 and 96.0 L mol^{-1} s^{-1} from the SEC and MALDI-MS curves of Figure 3, respectively. The SEC result underestimates the MALDI-MS result by about 5%. Although interference from a small miscalibration of especially the SEC apparatus can generally not be excluded—in particular when one is looking at MW accuracies of 5% or better—this difference is clearly, at least partly, a consequence of the fact that the polymer's MWD turns out significantly broader in SEC than in MALDI-MS. Compared with the SEC curve, the LMWSIP within the first PIO peak of the MALDI-MS curve appears at higher MW, while the high MW side inflection point (HMWSIP) appears at lower MW.

It has recently been proposed[5] that—for chain lengths of above, say, 50—the chain lengths at the *theoretical* LMWSIP within MWDs of PIO polymer might be estimated from chain lengths $i_{\max}$ at maxima within broadened *experimental* MWDs as $i_{\max} - i_{\max}^{0.5}$. In Figure 3, MWs at $M_M i_{\max}$ and $M_M(i_{\max} - i_{\max}^{0.5})$ have been indicated as bold and finely dotted vertical lines, respectively. Obviously the MW at $M_M(i_{\max} - i_{\max}^{0.5})$ matches the LMWSIP of the MALDI-MS signal almost perfectly, which corresponds to the expectation[5] that—within clearly resolved PIO peaks—theoretical and experimental LMWSIPs should be identical in the absence of broadening. The fact that MALDI-MS apparently underestimates the hypothetical theoretical LMWSIP to some very small extent would agree with the observation that even this advanced technique of measuring MWDs of polymers is not quite completely free of broadening errors (see above).

Since we chose LMWSIPs as best measures of k_p in Figure 3, it would be interesting to look for experimental situations where maxima within MWDs of PIO polymer might be a better choice. To this end one might think of increasing the energy of the initiating laser pulses which would correspond to an increase in the concentration of radicals produced per initiating pulse and thereby to a decrease in the radical concentration half-value life.[3,5] However, within our present experimental setup, 6 mJ cm^{-2} was already the maximum available EPAIMS for a homogeneous illumination of the reaction volume at a wavelength of 355 nm. Thus, in order to approach the high-termination rate limit, i.e., to make the radical concentration half-value life significantly shorter than the pulse period, we increased ΔT by 1 order of magnitude.

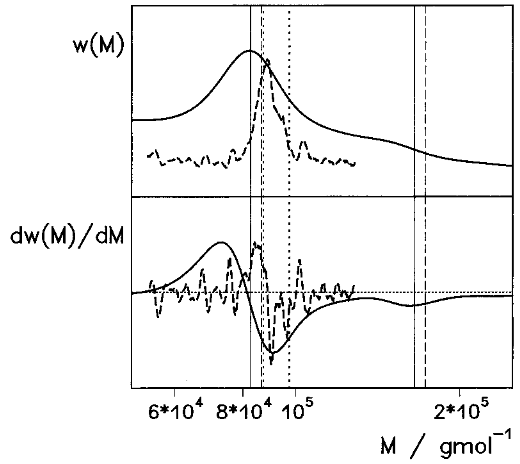

Figure 4. Experimental distributions $w(M)$ as obtained by means of SEC (full lines) or MALDI-MS (broken lines) together with numerically obtained derivatives d$w(M)$/dM thereof for a PLP of bulk S at 25 °C using laser pulses of an EPAIMS of 6 mJ cm^{-2} at 355 nm with a period of $\Delta T = 1.0$ s. Values of ordinates were plotted in arbitrary units against molecular weight M. Full and broken vertical lines correspond to the 10-fold molecular weights at LMWSIPs within SEC and MALDI-MS curves of Figure 3, respectively, and 2-fold multiples thereof, while bold and finely dotted vertical lines indicate the correspondingly scaled maximum and approximate theoretical LMWSIP. A value of d$w(M)$/d$M = 0$ is indicated as a horizontal dotted line.

Accordingly, Figure 4 shows weight representations $w(M)$ of MWDs obtained by means of SEC (full line) and MALDI-MS (broken line) together with corresponding derivatives d$w(M)$/dM with respect to MW M which, compared with the data shown in Figure 3, result from polymer produced under almost identical experimental conditions, except that the pulse period was altered from 0.1 to 1.0 s. Accordingly MWs appear roughly around 10^5 g mol^{-1} in Figure 4 rather than around 10^4 g mol^{-1} in Figure 3. The MWDs shown in Figure 4 contain one dominant PIO peak at around 8×10^4 g mol^{-1} and a shoulder of significantly lower weight fraction at around 1.6×10^5 g mol^{-1}. Within the MALDI-MS signal, only one sharp signal occurs shortly above 8×10^4 g mol^{-1}.

Full and broken vertical lines in Figure 4 do *not* correspond to the actual values of MWs at the LMWSIPs within the SEC and MALDI-MS curves *but* (for the purpose of direct comparison with the 10.0 Hz results) to the scaled values $10M_{\Delta T}$(10.0 Hz) and $20M_{\Delta T}$(10.0 Hz), respectively, where $M_{\Delta T}$(10.0 Hz) is in each case the MW at the LMWSIPs of the 10 Hz MWD of Figure 3 evaluated by means of SEC or MALDI-MS. The full vertical $10M_{\Delta T}$(10.0 Hz) line intersects the SEC signal almost perfectly at its maximum, while the broken vertical $10M_{\Delta T}$(10.0 Hz) line underestimates the maximum of the MALDI-MS signal by about 3%. These findings may be taken as an indication that the 1.0 Hz experiment evaluated in Figure 4 was performed in (or at least close to) the high-termination rate limit. This is all the more so as (1) in accordance with theory[3,5] the full vertical $20M_{\Delta T}$(10.0 Hz) line intersects the SEC signal fairly well at a minimum around $2M_{\max}$(1.0 Hz), where $M_{\max}$(1.0 Hz) corresponds to the actual maximum of the SEC curve in Figure 4, and (2) in any case tiny underestimation of the maximum of the MALDI-MS curve—being only moderately reliable due to the signal's poor S/N—is even further reduced by about 1% if we choose the theoretical LMWSIP of the 10.0 Hz experiment evaluated in Figure 3 as best estimate of k_p. (The fact that no polymer is observed at around 1.6×10^5 g mol^{-1} is certainly not of any significance but due to the

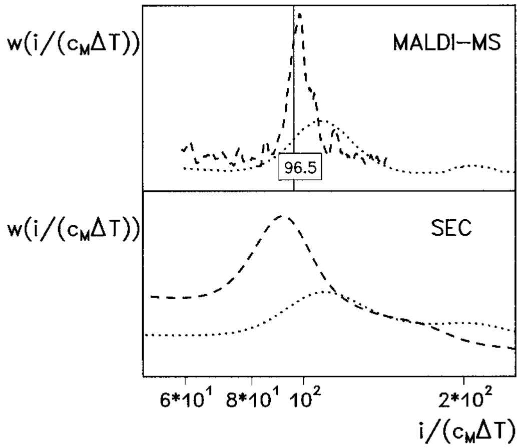

Figure 5. Experimental MWDs of Figures 3 and 4 replotted on an $i/(c_M\Delta T)$ scale with $i = M/M_M$. MALDI-MS and SEC results are shown in the upper and lower sections, respectively. Dotted and broken curves refer to 10.0 and 1.0 Hz experiments, respectively. The vertical line indicates the best estimate k_p value of 96.5 L mol^{-1} s^{-1} for bulk S at 25 °C.

insufficient sensitivity of MALDI-MS in this case.)

On the whole there appears to be clear evidence that the MWs at the LMWSIPs of the 10.0 Hz experiments shown in Figure 3 closely correspond to the MWs at the maxima of the 1.0 Hz experiments evaluated in Figure 4. For the purpose of more direct illustration of this observation, the experimental MWDs of Figures 3 and 4 are replotted on a $i/(c_M\Delta T)$ scale, that is, in terms of eq 1 and with $i = M/M_M$, on a "k_p scale", in Figure 5. Obviously only the MALDI-MS signal clearly shows the theoretically expected trend[3,5] of a decrease in the relative widths of PIO peaks with increasing chain length, that is, the 1.0 Hz MALDI-MS curve is significantly narrower than the corresponding 10.0 Hz curve. This neatly corroborates the recent supposition[5] that broadening errors in SEC increase with the chain length at which PIO peaks occur. Note that this would not necessarily mean that broadening errors in SEC generally increase with the chain length of polymers investigated but may simply reflect the decreasing relative widths of PIO peaks.

It should be noted that the absolute MW calibrations of the SEC and MALDI-MS results particularly in Figure 4, and correspondingly those of the 1.0 Hz results in Figure 5, are obviously not quite identical; in other words, the maxima of the SEC and MALDI-MS curves in Figure 4 are not identical. The reason for this finding is at present not clear. In view of the excellent agreement of SEC and MALDI-MS ensuing from Figure 1, one would hardly be inclined to attribute it to a miscalibration of the SEC, the MALDI-MS apparatus, or both. Perhaps there is some as yet not identified chromatographic problem related to the extent of broadening and occurring mainly at higher MWs (see below). At present we assume that MALDI-MS gives the more accurate results, particularly for the case of the 1.0 Hz experiment. This assessment relates *inter alia* to the observation that the MW $10M_{\Delta T}$(10.0 Hz) derived from the SEC curve in Figure 3 should give the lowest possible estimate for k_p in Figure 4 as it stems from a LMWSIP which probably contains some broadening error and as such should be a slight *underestimation* of its true value. Actually, however, it *overestimates* even the SEC curve's maximum in Figure 4 as does the corresponding $20M_{\Delta T}$(10.0 Hz) with respect to the minimum at $2M_{\max}$(1.0 Hz). Thus, from the given experimental data, we finally suggest a k_p value of 96.5 L mol^{-1} s^{-1} for bulk S at 25 °C. It fits well with the theoretical LMWSIP of both the MALDI-MS and SEC evaluations of the 10.0 Hz PLP and the maximum of the MALDI-MS evaluation of the 1.0 Hz PLP and is indicated as a vertical line in Figure 5. The value of 96.5 L mol^{-1} s^{-1} even exeeds the k_p of 92 L mol^{-1} s^{-1} given recently[3] for bulk S at 25 °C. This difference would appear to be plausible in that broadening impacts were not properly taken into account during evaluation of that recent value.

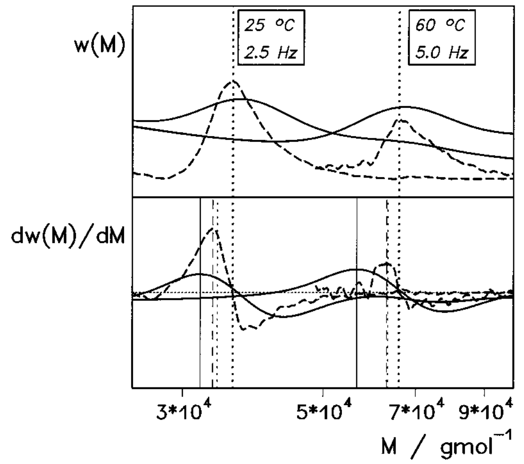

Figure 6. Experimental distributions $w(M)$ as obtained by means of SEC (full lines) or MALDI-MS (broken lines) together with numerically obtained derivatives $dw(M)/dM$ thereof for PLPs of bulk S using an EPAIMS of about 2 mJ cm^{-2} per pulse at 355 nm and a pulse period of 2.5 Hz at 25 °C (left) and a pulse period of 5.0 Hz at 60 °C (right). Values of ordinates were plotted in arbitrary units against molecular weight M. Full and broken vertical lines correspond to molecular weights at LMWSIPs within SEC and MALDI-MS curves, respectively. Dotted bold and fine vertical lines correspond to molecular weights at maxima and at approximate theoretical LMWSIPs within MALDI-MS curves. A value of $dw(M)/dM = 0$ is indicated as a horizontal dotted line.

Figure 6 shows MWD evaluations for PLPs of bulk S using pulses of an EPAIMS of about 2 mJ cm^{-2} at 355 nm with a period of 2.5 Hz at 25 °C and a period of 5.0 Hz at 60 °C, respectively. We shall look at the 25 °C results first: The SEC-derived LMWSIP (indicated as a full vertical line) gives a k_p of 88.0 L mol^{-1} s^{-1}, while the directly obtained LMWSIP of the MALDI-MS signal (indicated as a broken vertical line) and the corresponding maximum derived theoretical LMWSIP (indicated as a finely dotted vertical line) yield values of 93.0 and 94.5 L mol^{-1} s^{-1}, respectively. Obviously, the SEC-derived k_p significantly underestimates the best estimate of 96.5 L mol^{-1} s^{-1} given above, while the theoretical LMWSIP-derived value already compares excellently with it. The observed slight underestimation would agree with the notion that the low-termination rate limit was not quite entirely attained in this experiment, which would be plausible in view of the comparatively long pulse period of 0.4 s.

If we now look at the 60 °C results shown in Figure 6, however, it should be clear that the low-termination rate limit was more closely attained because of the considerable smaller pulse period of 0.2 s. Here the directly obtained LMWSIP of the MALDI-MS signal and the corresponding maximum derived theoretical LMWSIP give almost identical results for k_p. The value of 364 L mol^{-1} s^{-1} obtained in each case is again significantly underestimated by the MW at the SEC-derived LMWSIP (indicated as a full vertical line), which yields a k_p of 325 L mol^{-1} s^{-1}.

The results for the temperature-dependent k_p of bulk S are summarized at this point by suggesting best estimates of 96.5 L mol^{-1} s^{-1} for 25 °C and 364 L mol^{-1} s^{-1} at 60 °C which overestimate recently published bench-mark values of 86 and 341 L mol^{-1} s^{-1} at these temperatures[1] by about 12% and 7%, respectively. This "around 10%" underestimation—which a large body of experimental k_p data based on the PLP/MWD technique is probably containing, as a result of neglecting the impacts of instrumental broadening and termination rates on experimental MWDs—has already been predicted recently[5] but has now been considerably further substantiated for experiments with S.

Just to emphasize the precision of the present experimental MWD data, it might be noted in passing that the k_p values of 88.0 (at 25 °C) and 325 (at 60 °C) L mol^{-1} s^{-1} derived from the LMWSIPs of the SEC signals shown in Figure 6 compare really well with the above bench-mark value. This agreement shows the general consistency of the basic PLP/MWD data—i.e., those behind the bench-mark data[1] and those obtained during the present investigation—in the sense that choosing LMWSIPs within MWDs obtained by SEC as best measures for k_p has been common practice in former investigations.

SEC/MALDI-MS Comparison of PLP/MWD Results for the Methyl Methacrylate k_p. The above-mentioned UV-spectroscopic control of the absorptions of the reaction mixtures to ≤0.5 at the respective laser wavelengths was performed in order to avoid all-too-steep gradients of laser energy (and quasi-instantaneous radical concentrations thereby produced) across the irradiated monomer layers. While such a control is essential for polymerizations of 10 mm layers of S (even at wavelengths of 355 nm or higher), it is considerably less important for 10 mm layers of MMA (even at wavelengths of 308 nm). Thus, for the polymerization of MMA, a maximum EPAIMS of about 150 mJ cm^{-2} was available at 308 nm. This maximum energy per pulse was optionally attenuated to roughly 1/100 to show the impact of varying concentrations of pulse-produced radicals, i.e., of varying radical concentration halflife values, on the overall appearances of MWDs.

Figure 7 shows experimental distributions $w(M)$ obtained by means of SEC (full lines) or MALDI-MS (broken lines) together with corresponding derivatives d$w(M)$/dM for a PLP of bulk MMA at 25 °C using laser pulses of a period of $\Delta T = 0.1$ s with an EPAIMS of about 150 mJ cm^{-2} (bold lines) or 2 mJ cm^{-2} (fine lines) at 308 nm. The MWDs resulting from polymer produced with high-energy laser pulses contain a dominant first PIO peak at around 3.5 × 10^4 g mol^{-1}. As with the results obtained for S, the MWs at the maximum of this peak obtained by means of SEC and MALDI-MS agree excellently with one another, while the width of the SEC curve is again considerably broader than the width of the MALDI-MS curve.

According to the theory,[3] only a shoulder instead of a dominant PIO peak is expected within MWDs resulting from polymer produced with laser pulses of correspondingly low energy. The low-laser energy SEC curve of Figure 7 obviously agrees with this expectation, while the low-laser energy MALDI-MS curve does not. Instead, even the low-laser energy MALDI-MS curve shows a PIO peak. The origin of the evolution of this peak, whose MW position agrees remarkably well with the high-laser energy PIO peak, is currently assumed to result from an underestimation of higher MW species relative to lower MW species but will not be discussed further because of insufficient MALDI-MS data.

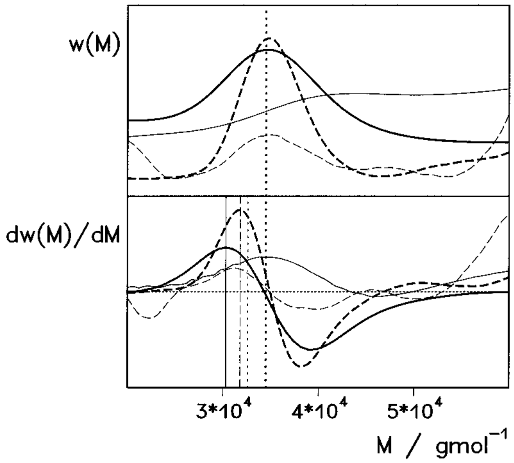

Figure 7. Experimental distributions $w(M)$ as obtained by means of SEC (full lines) or MALDI-MS (broken lines) together with numerically obtained derivatives d$w(M)$/dM thereof for a PLP of bulk MMA at 25 °C using laser pulses of a period of $\Delta T = 0.1$ s with an EPAIMS of about 150 mJ cm^{-2} (bold lines) or 2 mJ cm^{-2} (fine lines) at 308 nm. Values of ordinates were plotted in arbitrary units against molecular weight M. Values of molecular weights at the LMWSIPs of these MWDs have been indicated as full and broken vertical lines for SEC and MALDI-MS curves, respectively. Values of molecular weights at the maximum and at the approximate theoretical LMWSIP of the dominating PIO peak are indicated as dotted bold and fine vertical lines, respectively. A value of d$w(M)$/dM = 0 is indicated as a horizontal dotted line.

Values of MWs at the LMWSIPs of the high-energy MWDs in Figure 7 have again been indicated as full and broken vertical lines for SEC and MALDI-MS curves, respectively; values of MWs at the maximum of the high-energy MWDs and at the corresponding theoretical LMWSIP are again indicated as dotted bold and fine vertical lines. The theoretical LMWSIP calculated from the peak maximum's MW again compares quite favorably with the experimental LMWSIP of the MALDI-MS signal, while, as above, the former actually overestimates the latter slightly. However, the theoretical LMWSIP is not taken as best estimate of k_p in this case because, as required for this selection,[3] the high-laser energy MWDs are not in the low-termination rate limit. Particularly from the results obtained by SEC we may contrarily assume that the high-laser energy MWD is close to the high-termination rate limit because of the obvious agreement of the MW of its maximum with the LMWSIP of the low-laser energy MWD.[3] Thus we suggest a best estimate of k_p = 372 L mol^{-1} s^{-1} for the free-radical polymerization of MMA in bulk at 25 °C deduced from both of the maxima of the high-laser energy MWD and the LMWSIP of the low-laser energy MWD in Figure 7. As with the k_p of S above, this value exceeds the k_p of 359 L mol^{-1} s^{-1} given recently[3] for bulk MMA at 25 °C. As above, this difference may be rationalized in that the influence of instrumental broadening was not properly accounted for during evaluation of the former value.

Finally, MWDs obtained for a PLP of MMA at 60 °C are shown in Figure 8. Qualitatively these results resemble those shown for 25 °C in Figure 7 almost completely, except that no evaluable MALDI-MS signal could be measured for the low-laser energy experiment. Compared to Figure 7, where PIO MWD characteristics appear around 3.5 × 10^4 g mol^{-1}, the width of the high-laser energy SEC result in Figure 8 overestimates the width of the corresponding MALDI-MS curve appearing at around 8.6 × 10^4 g mol^{-1} even more. Once again, theoretical and experimental LMWSIPs within the

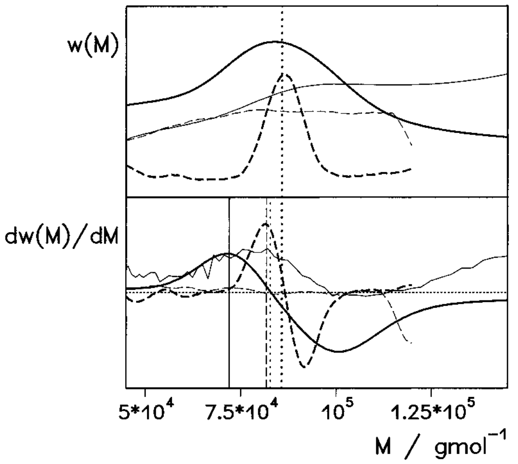

Figure 8. Experimental distributions $w(M)$ as obtained by means of SEC (full lines) or MALDI-MS (broken lines) together with numerically obtained derivatives $\mathrm{d}w(M)/\mathrm{d}M$ thereof for a PLP of bulk MMA at 60 °C using laser pulses of a period of $\Delta T = 0.1$ s with an EPAIMS of about 150 mJ cm^{-2} (bold lines) or 2 mJ cm^{-2} (fine lines) at 308 nm. Values of ordinates were plotted in arbitrary units against molecular weight M. Values of molecular weights at the LMWSIPs of these MWDs have been indicated as full and broken vertical lines for SEC and MALDI-MS curves, respectively. Values of molecular weights at the maximum and at the approximate theoretical LMWSIP of the dominating PIO peak are indicated as dotted bold and fine vertical lines, respectively. A value of $\mathrm{d}w(M)/\mathrm{d}M = 0$ is indicated as a horizontal dotted line.

MWD obtained for the high laser energy by means of MALDI-MS compare remarkably well with one another. Like the 25 °C results for S in Figure 4, the absolute MW calibrations of the SEC and MALDI-MS results in Figure 8 are apparently not quite identical. As above, we prefer to believe the absolute MWs obtained by mass spectrometry rather than those obtained by chromatography. Thus, while we may deduce from a comparison of high- and low-laser energy SEC results, along the same lines as for the 25 °C results, that the high-laser energy experiment evaluated in Figure 8 was performed close to the high-termination rate limit, we suggest a best estimate of $k_p = 962$ L mol^{-1} s^{-1} for the free-radical polymerization of MMA in bulk at 60 °C from the maximum of the high-laser energy MWD of Figure 8 obtained by MALDI-MS.

Both the above-mentioned results of $k_p = 372$ L mol^{-1} s^{-1} at 25 °C, as well as that of $k_p = 962$ L mol^{-1} s^{-1} at 60 °C, overestimate recently published bench-mark values of 323 and 833 L mol^{-1} s^{-1} at these temperatures[2] by about 15%. This difference again fulfills the recent prediction already mentioned above,[5] which now appears to be substantiated also for experiments with MMA. It goes without saying that—also as expected—the k_p values deduced for 25 and 60 °C from the LMWSIPs of what we have called "high-laser energy MWDs" of Figures 7 and 8 of 326 and 812 L mol^{-1} s^{-1} excellently agree with the above bench-mark values.

Conclusions

Even for PS and PMMA where, compared to many other polymers, disproportionately accurate determinations of MWDs are possible by SEC due to the availability of well-characterized MW standards, the suitability of MALDI-MS for measuring absolute MWDs seems to outperform the suitability of the former in efforts to obtain most accurate values of propagation rate coefficients for free-radical polymerizations. This will be the case particularly when absolute MWs of co- or multipolymers or branched polymers are to be investigated because well-characterized MW standards for the calibration of SEC are generally lacking in these instances. With respect to determinations of accurate k_p values from MWDs of pulsed-laser-made polymer, an additional advantage of MALDI-MS over SEC is the extent of broadening errors of experimental MWDs, which are significantly smaller in MALDI-MS than in SEC. It appears that, especially for *relatively narrow* high-termination rate MWDs (e.g., those of the present investigation, which contain only one dominant PIO peak of a polydispersity of about 1.05 or below), reliable MWD data may be obtained with state-of-the-art MALDI-MS equipment. While MALDI-MS methods certainly need to be improved with special respect to reliable measurements of significantly *broader* MWDs, and although the character of the present study should be understood as being more explorative than exhaustive, the great potential of this young analytical tool—whose capabilities to provide MWDs of polymers has just recently[16] been extended to 430 000 g mol^{-1}—is clearly evident.

Abbreviations

S, styrene; MMA, methyl methacrylate; MWD, molecular weight distribution; SEC, size exclusion chromatography; MALDI-MS, matrix-assisted laser desorption/ionization mass spectrometry; PLP, pulsed-laser polymerization; MW, molecular weight; S/N, ratio of signal to noise; PS, polystyrene; PMMA, poly(methyl methacrylate); EPAIMS, energy per area of illuminated monomer surface; LMWSIP, low MW side inflection point; PIO, pulsed-initiation-originating.

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