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Matrix-assisted laser desorption/ionization mass spectrometry of synthetic polymers: 2. Analysis of poly(methyl methacrylate)

Harald Pasch*
Deutsches Kunststoff-Institut, Schlossgartenstrasse 6, 64289 Darmstadt, Germany

and Friedhelm Gores
Polymer Standards Service GmbH, Wöhlerstrasse 2–6, 55023 Mainz, Germany
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Matrix-assisted laser desorption/ionization mass spectrometry (m.a.l.d.i.-m.s.) is shown to be a unique method for the determination of the functional heterogeneity of poly(methyl methacrylate)s. In group-transfer polymerization of methyl methacrylate, oligomers with cyclic end-groups are formed in addition to the expected linear oligomers. The cyclics are identified via preparative separation of the cyclic trimer by high-performance size exclusion chromatography. Using m.a.l.d.i.-m.s. the different homologous series are identified and their molar-mass distributions are calculated. In addition, high-performance size exclusion chromatography with dual refractive-index and ultra-violet detection provides information on the molar-mass distribution of the cyclic fraction. For technical products, it is shown that oligomers with cyclic end-groups may be formed in significant amounts and, therefore, have to be accounted for in structural characterization.

(Keywords: mass spectrometry; m.a.l.d.i.-m.s.; poly(methyl methacrylate))

INTRODUCTION

Group-transfer polymerization (g.t.p.) is an interesting new technique for the preparation of polymethacrylates. In this technique a silyl ketene acetal initiator reacts with a monomer by a Michael addition. During the addition, the silyl group transfers to the monomer, generating a new ketene acetal function[1–3]. In this way 'living' polyacrylics are formed at ambient temperatures. To control the molar mass, it is essential that the rate of initiation be higher than or the same as the rate of propagation. Therefore, the best initiators will be similar in structure to the living end of the polymer. Thus, for methacrylate g.t.p. a silyl ketene acetal with an alkyl group in the 2 position is ideal.

The molar masses of polymethacrylates obtained by g.t.p. are determined by the molar ratio of initiator to monomer. The molar-mass distribution M_w/M_n for g.t.p. polymers under the best conditions is close to 1. Polymers with reactive functionality on one end are useful tools for synthesis of graft copolymers, dispersing agents and ABA block copolymers. To make sure that copolymers with strictly predetermined structures are formed, a functionality analysis of the precursor polymers is necessary.

Mass spectrometry has become a viable technique for characterization of low-molar-mass synthetic polymers. The power of mass spectrometry is the fast and accurate determination of molar masses, the sequence of repeat units, polymer additives and impurities. The main barriers for mass spectrometry of high-molar-mass compounds, caused by the low volatility and thermal instability of polymers, have been overcome by the development of soft ionization techniques, such as secondary-ion mass spectrometry[4,5] and field desorption[6,7]. CO_2-laser desorption, combined with either a time-of-flight or a Fourier-transform mass analyser, yields molecular-ion peaks for a number of polymers with relative molecular mass up to 10 000[8,9].

A new, most promising method for the separation of large molecules according to their molar mass and functionality has been introduced recently. Matrix-assisted laser desorption/ionization mass spectrometry (m.a.l.d.i.-m.s.), developed by Karas and Hillenkamp in 1988[10], has been successfully used to determine the mass of large biomolecules and synthetic polymers[11,12]. The accessible mass range has been extended considerably, and the technique is fast and instrumentally very simple. Moreover, relatively inexpensive commercial instrumentation has become accessible. In principle, the sample to be investigated and a matrix solution are mixed in such a ratio that matrix separation of the sample molecules is achieved. After drying, a laser pulse is directed onto the solid matrix to photo-excite the matrix material. This excitation causes the matrix to explode, resulting in the expulsion and soft ionization of the sample molecules without fragmentation. Once the analyte is ionized, it is

* To whom correspondence should be addressed

accelerated and analysed in a time-of-flight (t.o.f.) mass spectrometer. As a result, the analyte is separated according to the molar mass of its components, and in the case of heterogeneous polymers a molar-mass distribution may be obtained. In a number of papers it was shown that technical polymers may be analysed up to relative molecular masses of about 200 000[13,14]. Recently, it was shown by us that epoxy resins may be separated into their oligomers according to the degree of polymerization and the type of functional groups[15].

In the present report a number of poly(methyl methacrylate)s (PMMA) are investigated with respect to their molar mass and functionality using m.a.l.d.i.-m.s. It will be demonstrated that different homologous series are obtained, indicating functional heterogeneity of the samples.

EXPERIMENTAL

Samples

Samples 1–3 and 7 are poly(methyl methacrylate) calibration standards (Polymer Standards Service, Mainz). Samples 4 and 5 were synthesized by group-transfer polymerization at Röhm Chemische Fabrik, Darmstadt. Sample 6 was prepared by radical polymerization at Röhm Chemische Fabrik, Darmstadt.

M.a.l.d.i.-m.s.

The m.a.l.d.i.-m.s. investigations were conducted on a Kratos Kompact MALDI 3. The samples were dissolved in tetrahydrofuran (THF) or acetone and mixed with the matrix 2,5-dihydroxybenzoic acid. After drying the mixture of the sample and the matrix on the sample holder, the measurements were carried out using the following conditions: polarity—positive; flight path—reflection; mass—high (20 kV acceleration voltage); 100 shots per sample.

Size exclusion chromatography

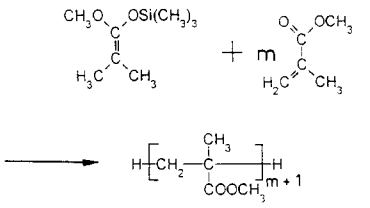
The s.e.c. experiments were conducted on a Waters modular s.e.c. system. The solvent was THF, and a column set of six Waters Ultrastyragel columns (3 × 100 Å, 2 × 500 Å, 1000 Å) was used. The detector was a Waters 410 differential refractometer.

High-performance s.e.c.

The high-performance s.e.c. separations were conducted on a modular system, comprising a SP IsoChrom HPLC pump, a Shodex SE 71 differential refractometer and a SP 8450 UV/VIS detector (300 nm). The solvent was THF, and a column set of two PSS-SDV 100 Å, 600 × 8 mm i.d., columns was used.

RESULTS AND DISCUSSION

The PMMA samples were prepared by g.t.p. according to the reaction shown in *Scheme 1*. Accordingly, the resulting polymers consist of the PMMA chain without any end-group and a heterogeneity in the end-group functionality is not to be expected. The corresponding size exclusion chromatograms show nice oligomer separations for the lower-molar-mass samples and uniform elution profiles for the higher-molar-mass samples (see *Figure 1*). In agreement with the theory, the



Scheme 1 Reaction scheme of the group-transfer polymerization

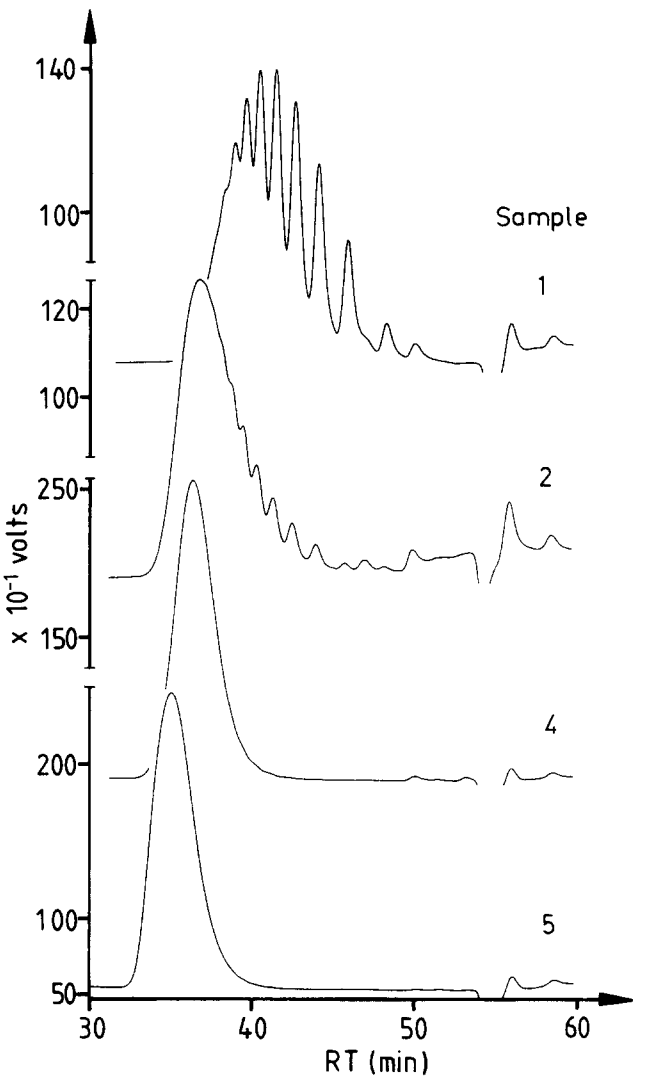


Figure 1 S.e.c. chromatograms of poly(methyl methacrylate)s prepared by g.t.p.: stationary phase, Ultrastyragel; eluent, THF

molar-mass distributions of the samples are very narrow. The shape of the elution curves does not indicate any functional heterogeneity.

The m.a.l.d.i.-m.s. spectrum of a PMMA calibration standard of nominal peak maximum molar mass of 720 g mol^{-1} (sample 1), prepared by g.t.p., is given in *Figure 2*. For sample preparation in the m.a.l.d.i.-m.s. experiment the PMMA is dissolved in THF and mixed with dihydroxybenzoic acid as the matrix. In order to promote ionization, a small amount of LiCl is added to the sample. The spectrum consists of a number of peaks of different intensity having a peak-to-peak mass increment of 100 g mol^{-1}. This mass increment exactly equals the mass of the repeat unit in PMMA and, therefore, each peak represents one oligomer in the

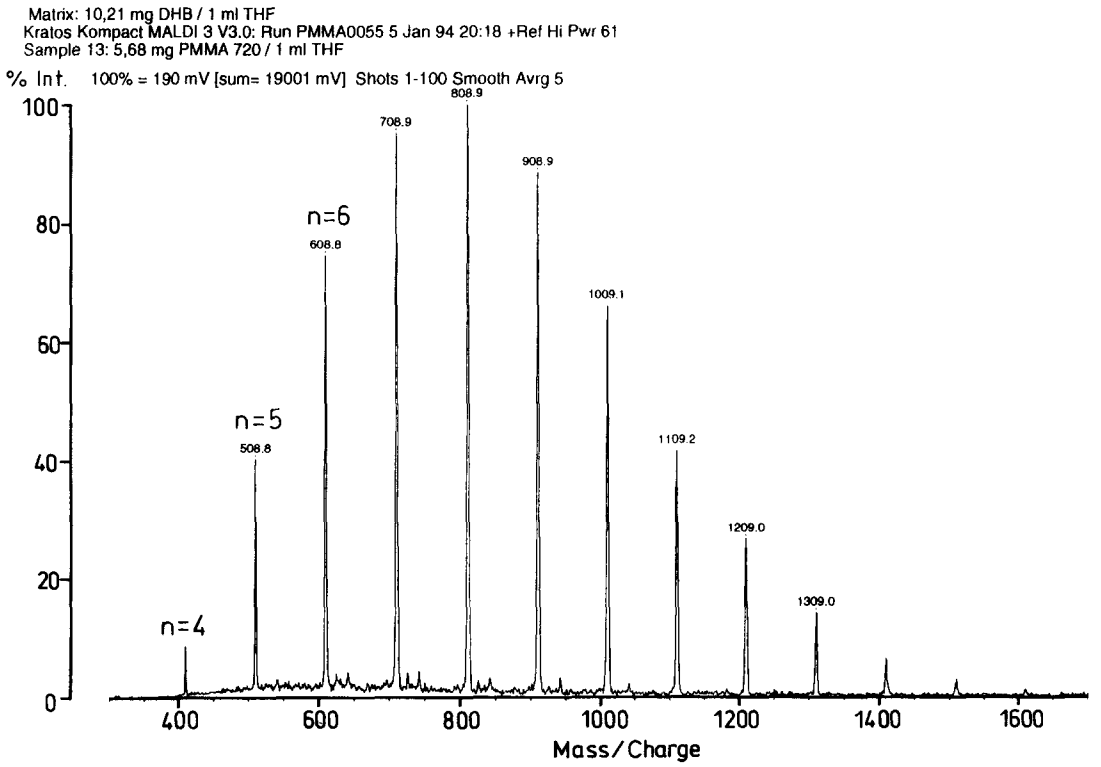


Figure 2 M.a.l.d.i.-m.s. spectrum of a PMMA calibration standard (sample 1); *n*-degree of polymerization

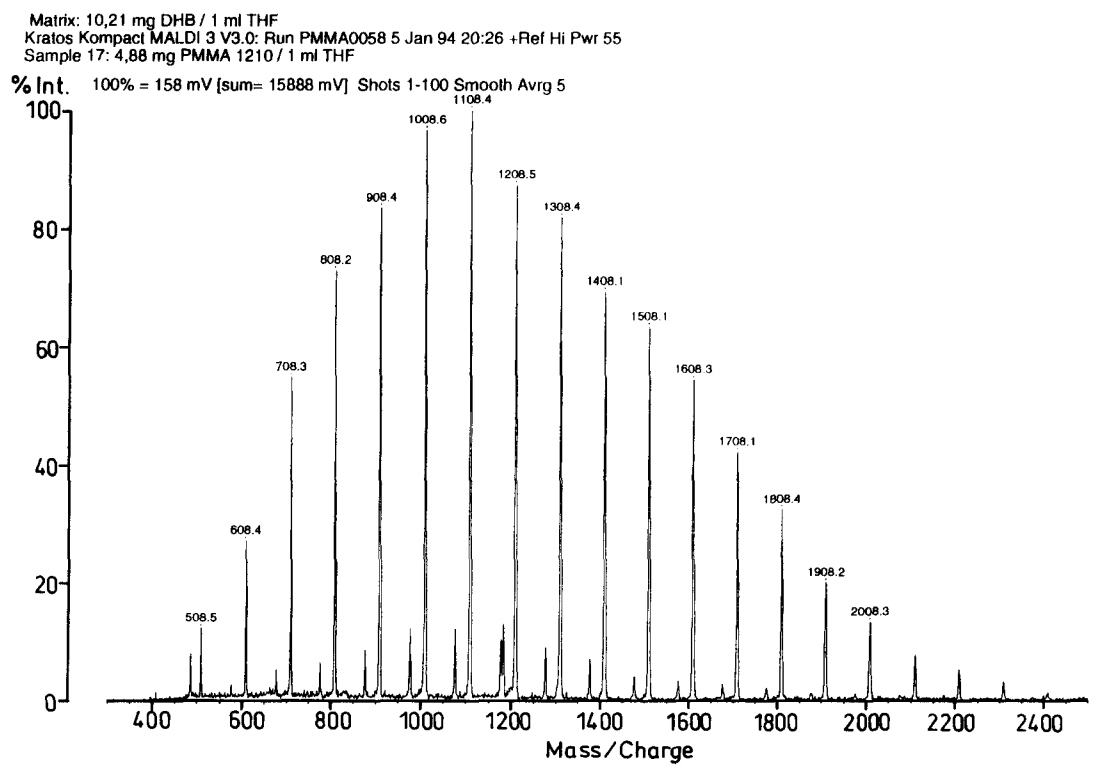


Figure 3 M.a.l.d.i.-m.s. spectrum of a PMMA calibration standard (sample 2)

oligomer mixture. The peaks are due to the intact $M + Li^+$ molecular ions, which are formed by the attachment of Li^+ from the substrate to the oligomers. Accordingly, the masses of the oligomers correspond to $M + Li^+ = 9 + 100n$, n being the degree of polymerization. By definition, this homologous series is called the 'linear fraction'. As can be seen from the spectrum, there is no indication of other functionalities. The very small additional peaks in the spectrum are due to the formation of $M + Na^+$ and $M + K^+$ molecular ions.

The inspection of the m.a.l.d.i.-m.s. spectrum of a PMMA with a molar mass of 1210 g mol^{-1} (sample 2) reveals that, in addition to the peaks of the linear fraction, a number of peaks of lower intensity are obtained (see *Figure 3*). These peaks also have a peak-to-peak mass increment of 100 g mol^{-1}, indicating that they belong to

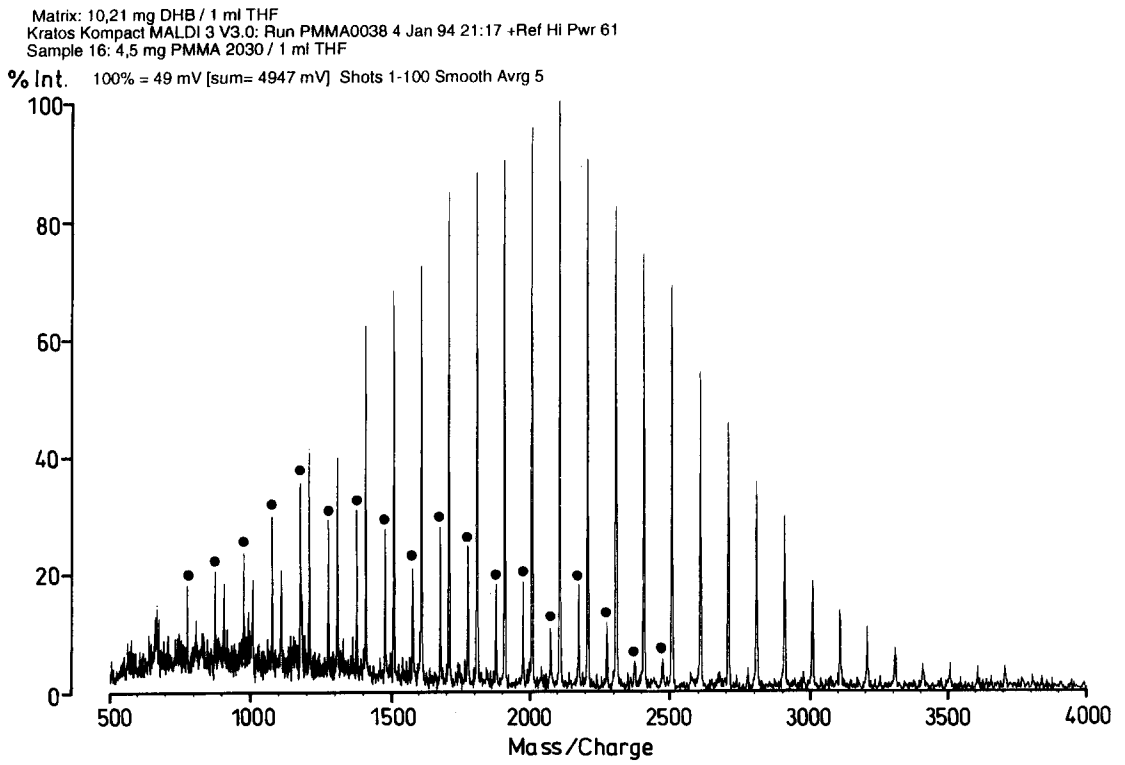


Figure 4 M.a.l.d.i.-m.s. spectrum of a PMMA calibration standard (sample 3); full circles indicate the cyclic oligomers

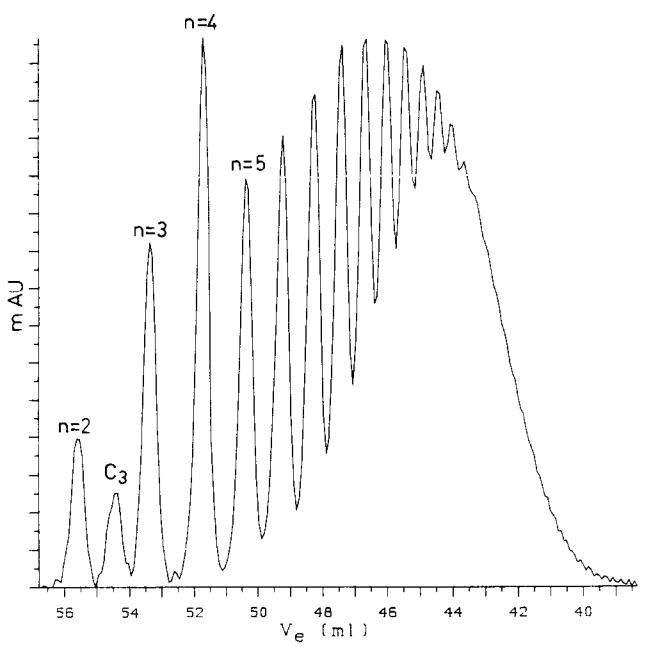


Figure 5 H.p.s.e.c. chromatogram of PMMA sample 7: stationary phase, cross-linked polystyrene; eluent, THF; *n*-degree of polymerization; C_3, cyclic trimer

a second PMMA-based homologous series. The mass difference between both series is about 31 g mol^{-1}. As the mass increment of both homologous series is the same, the changes in the chemical structure must be attributed to variations in the end-group. The fact that both homologous series have their maximum abundance at about 1100 g mol^{-1} indicates that they are formed simultaneously in the reaction. For a PMMA sample of higher molar mass (PMMA 2030, sample 3) the molar-mass distributions of the homologous series are quite different (see *Figure 4*). While the most abundant peak of the linear fraction appears at about 2100 g mol^{-1}, the most abundant peak of the second homologous series is at about 1200 g mol^{-1}. This might indicate a molar-mass effect in the formation of this series.

In order to investigate the nature of the second homologous series, a PMMA sample is separated into its oligomers by high-performance s.e.c. (see *Figure 5*). The chromatogram shows the expected separation into the oligomers up to a degree of polymerization of about $n = 15$. In addition to the peaks of the linear oligomers, a peak at $V_e = 54.5$ ml is obtained, which is attributed to the cyclic MMA trimer. This peak is separated preparatively and subjected to m.a.l.d.i.-m.s. giving a peak for the $M + Li^+$ molecular ion at 278 g mol^{-1}. The same peak appears in the m.a.l.d.i.-m.s. spectrum of the initial PMMA and gives a mass increment to the linear trimer of about 31 g mol^{-1}. Further peaks of low intensity appear at 778, 878, 978 g mol^{-1} and so on (see *Figure 6*). The coincidence of this series of peaks with the second homologous series in the previous samples is obvious. Therefore, this homologous series must be attributed to the formation of cyclic structures in addition to the main linear fraction. Accordingly, the second homologous series by definition is called the 'cyclic fraction'.

The investigation of the functional heterogeneity of two technical poly(methyl methacrylate)s prepared by g.t.p. is given in *Figure 7*. Similar to the previous samples, two homologous series with a peak-to-peak mass increment of 100 g mol^{-1} and a mass difference of 31 g mol^{-1} are obtained. Accordingly, these series can be assigned to the linear and the cyclic fractions, as was

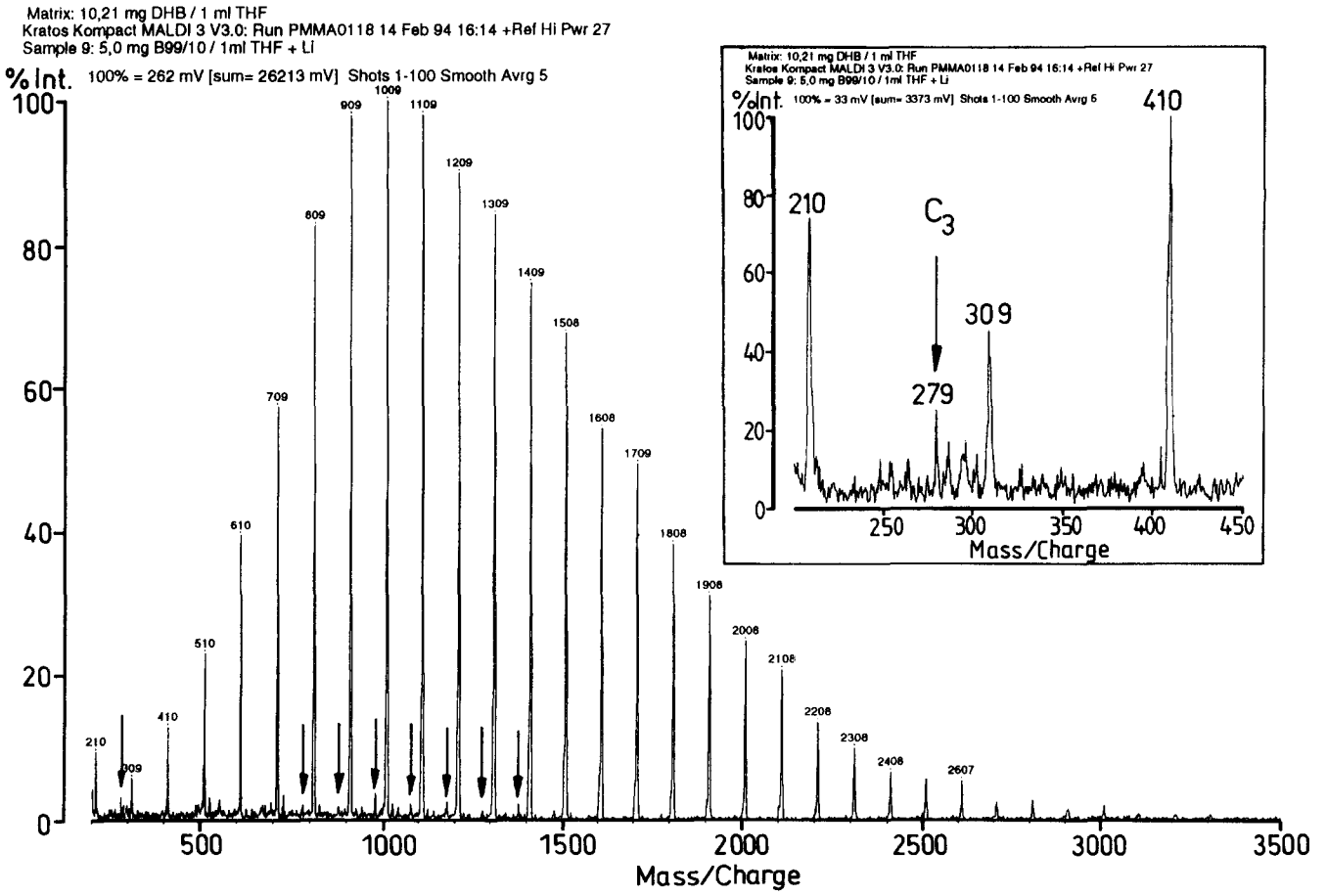


Figure 6 M.a.l.d.i.-m.s. spectrum of PMMA sample 7; arrows indicate the cyclic oligomers

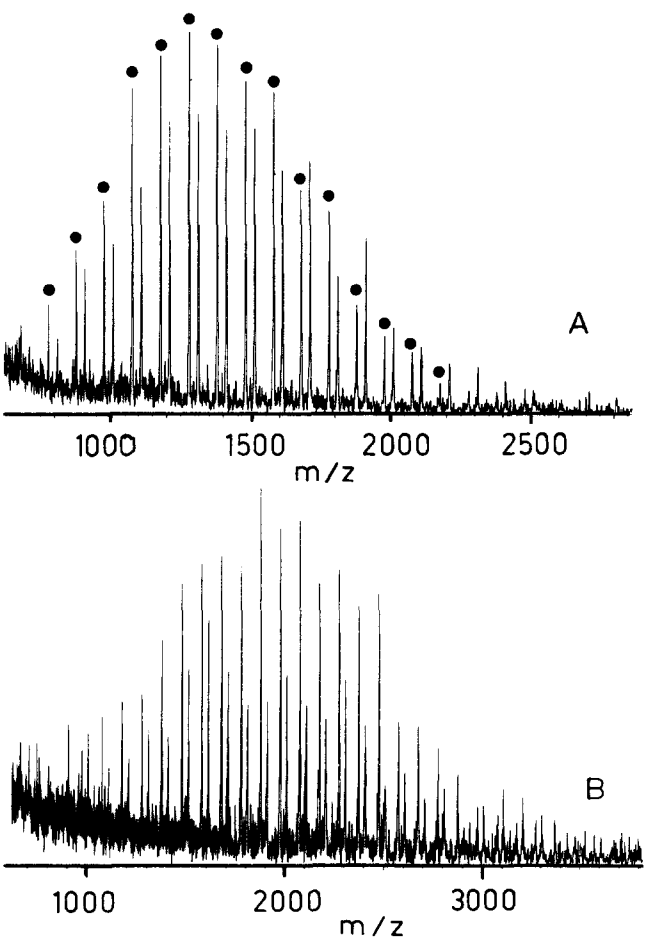


Figure 7 M.a.l.d.i.-m.s. spectra of technical poly(methyl methacrylate)s prepared by g.t.p.; full circles indicate the cyclic oligomers; A, sample 4; B, sample 5

discussed before. However, for these samples the intensity of the peaks of the cyclic fraction is higher compared to the linear fraction. The formation of cyclic end-groups in the technical g.t.p. process seems to play an important role and, therefore, has to be accounted for in the characterization.

In order to obtain additional information on the functional heterogeneity of samples 4 and 5, these samples are subjected to high-performance s.e.c. with dual r.i. and u.v. detection. The u.v. detector is adjusted to a wavelength of 300 nm, where the linear oligomers do not absorb light. Owing to the keto ester structure of the cyclic end-group, these oligomers have an absorption maximum at about 300 nm. Therefore, the u.v. trace selectively represents the molar-mass distribution of the cyclic fraction, whereas the r.i. trace characterizes the whole sample[16] (see *Figure 8*). As can be seen from the retention times of the peaks, there is virtually no difference between the u.v. and the r.i. traces. Thus, the cyclic and linear oligomers with $n \geqslant 4$ elute at the same elution time and chromatographically cannot be separated from each other.

Molar-mass determinations from m.a.l.d.i.-m.s. spectra can be made by taking into account the intensity of the oligomer signals and the mass at which they arise. The molar masses of the linear and cyclic fraction data are listed in *Table 1*. Following the previous discussion on

Table 1 Molar-mass data of the PMMA samples from s.e.c. and m.a.l.d.i.-m.s.

	S.e.c.		M.a.l.d.i.-m.s.			H.p.s.e.c.		
Sample	M_n	M_w		M_n	M_w		M_n	M_w
1	570	690		820	880			
2	900	1140	linear	1200	1310			
			cyclic	1000	1130			
3	1800	2000	linear	1900	2110			
			cyclic	1310	1500			
4	1320	1460	linear	1450	1530	total	1220	1330
			cyclic	1190	1300	cyclic	1040	1160
5	1810	2080	linear	1850	1970	total	1690	1860
			cyclic	1740	1900	cyclic	1620	1730
6	1420	1700		1230	1450			

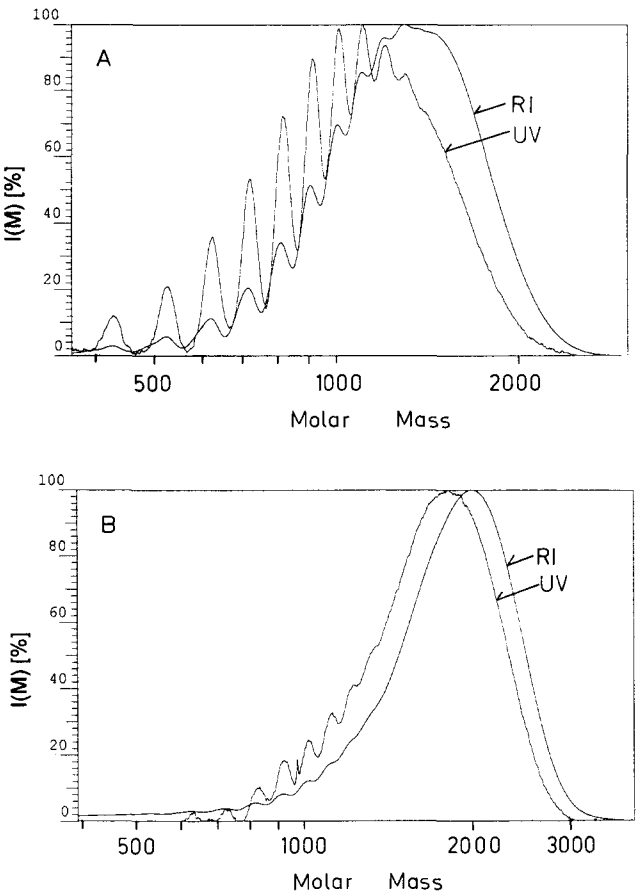
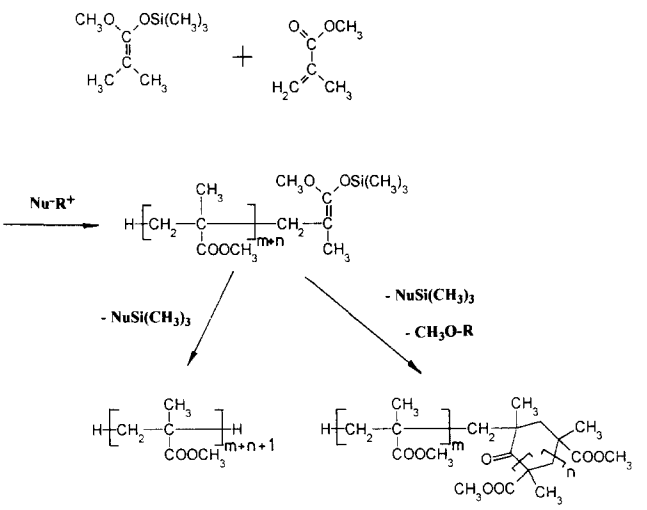


Figure 8 H.p.s.e.c. chromatograms of samples 4 (A) and 5 (B); for experimental conditions, see *Figure 5*

the detector response, from the u.v. trace of the h.p.s.e.c. chromatograms the molar-mass distribution of the cyclic fractions may be calculated. From the r.i. trace the total molar-mass distribution of the samples is available. As can be seen, a good agreement of the data from different techniques is obtained. The fact that the m.a.l.d.i.-m.s. numbers for the cyclics are gradually increased compared to h.p.s.e.c. (see samples 4 and 5) might be due to a significant noise level in the low-mass region of the m.a.l.d.i.-m.s. spectra, which makes it difficult for the software to recognize all peaks.

Different from g.t.p. polymerized samples, PMMA prepared by radical polymerization does not have this



Scheme 2

functional heterogeneity. *Figure 9* shows the oligomer distribution of a hydroxy-terminated PMMA, which was prepared by radical polymerization. Although two peaks are obtained for each degree of polymerization, these peaks have a mass difference of 16 g mol^{-1} and must be assigned to the $M + Na^+$ and $M + K^+$ molecular ions, respectively.

In conclusion, the reaction scheme shown in *Scheme 2* reflects the simultaneous formation of a linear and a cyclic fraction in the group-transfer polymerization of methyl methacrylate. The cyclic fraction consists of linear oligomers with cyclic end-groups, which are formed in a back-biting reaction of the reactive silyl end-groups and the ester groups of its own polymer chain. The size of the cyclic end-groups cannot be determined, but for steric reasons it is assumed to be rather small. In anionic and g.t.p. polymerization of methyl methacrylate, only six-membered rings have been found[17,18]. The reason for an increased cycle content in the technical PMMA samples is given by a competitive reaction of the reactive chain end with either monomer or back-biting. After completed monomer consumption only back-biting can occur at the end of the polymerization reaction. M.a.l.d.i.-m.s. has been shown to be a unique method for the identification of this type of functional heterogeneity and the determination of the molar-mass distributions of the linear and cyclic fractions.

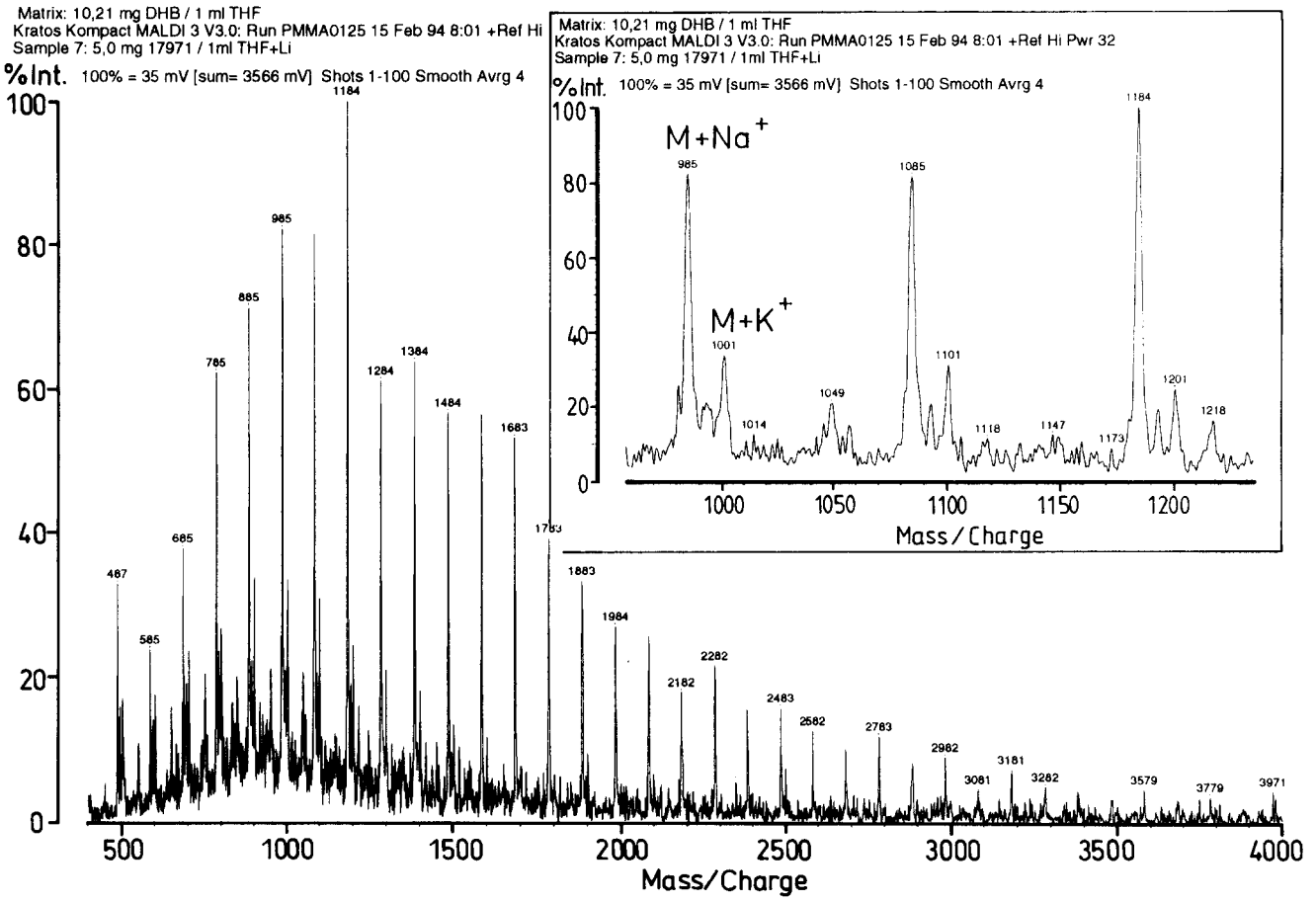


Figure 9 M.a.l.d.i.-m.s. spectrum of PMMA sample 6 prepared by radical polymerization

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