Electrospray ionization mass spectrometric end-group analysis of PMMA produced by radical polymerization using diacyl peroxide initiators

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Abstract

The type and number of end groups of poly(methyl methacrylates) from free-radical polymerization with six diacyl peroxides, R−(CO)O−O(CO)−R, acting as initiators have been analyzed via electrospray ionization mass spectrometry using an ion trap and additionally Fourier transform ion cyclotron resonance for mass detection. The polymerizations were carried out in benzene solution at high initiator concentration to yield low molecular weight polymer. With R being an alkyl group, only R moieties are observed as end groups. For each oligomer size, molecules with one or two such end groups are formed, depending on whether termination occurs via disproportionation or combination. With R being an aryl type, as in di-benzoyl and di-naphthoyl peroxides, both R and R−(CO)O moieties are detected as polymeric end groups. Because of aromatic delocalization, fractions of the arylic R−(CO)O[.] radicals are sufficiently long living at 95 °C to add to a monomer molecule prior to undergo decarboxylation.
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1. Introduction

Electrospray ionization mass spectrometry (ESI-MS) has proven to be a powerful tool for end-group analysis [1] of polymers produced by laser initiation [2−4] and controlled radical polymerization [5−9]. The technique has recently been extended to investigations on the initial growth step of radical polymerizations initiated by alkyl peroxypivalates [10] and peroxyacetates [11]. The potential of ESI-MS for exploring mechanistic aspects of radical polymerization has been highlighted in a feature article [12] and the impact of ESI-MS on the characterization of synthetic polymers has been reviewed [13−20]. The ESI process is gentle in comparison with other ionization techniques used in conjunction with MS [21]. As a consequence, fragmentation of the analyte molecules may be avoided and mass spectrometric information on the macromolecules of interest becomes available. This feature makes ESI-MS highly suitable for end-group analysis of polymer produced under well-defined reaction conditions. Synthetic polymers, however, mostly consist of macromolecules which largely differ in size. Thus a multitude of ESI-MS signals occurs even without any fragmentation. In case of multiple ionization, which is frequently observed with ESI, the situation may be even more complex and MS techniques that employ common mass analyzers with low mass resolution, such as an ion trap, a quadrupole mass filter, and linear time-of-flight analyzers, suffer from serious peak overlap. Such overlap may be avoided by using Fourier transform ion cyclotron resonance (FT-ICR) for mass detection, which provides a very high mass resolution of about 100,000 using broadband excitation. Additionally, the highly accurate mass measurement of FT-ICR MS enormously facilitates the unambiguous determination of the elemental composition of analytes [22,23].

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In combining conventional low resolution ESI-MS and FT-ICR mass analysis, the present study aims at the accurate characterization of the end groups of poly(methyl methacrylate), poly(MMA), produced by chemically induced solution polymerization using the following diacyl peroxide initiators: di-*n*-decanoyl peroxide (DDP), di-*n*-dodecanoyl peroxide (DDDP), bis(3,5,5-trimethylhexanoyl)peroxide (BTMHP), di-*iso*-butyryl peroxide (DIBP), di-benzoyl peroxide (DBPO), and di-2-naphthoyl peroxide (D2NPO) (see Chart 1).

Aliphatic and aromatic diacyl peroxides were selected because of the differences in decarboxylation rate of the primary fragments from peroxide decomposition. As shown by recent DFT estimates [24–28], decarboxylation of aryl carbonyloxy radicals is relatively slow, as this process is associated with a reduction of the range of electron delocalization. End-group analysis on polymeric products should reveal whether and to which extent decarboxylation of the primary initiator-derived radical fragment occurs prior to the addition of the first monomer molecule and by which process chain growth starts.

Illustrated in Scheme 1 is a general representation of the decomposition of symmetric diacyl peroxides. The primary decomposition step yields two identical oxygen-centered radicals **X**, which may decarboxylate yielding the carbon-centered alkyl or aryl radicals **y**. To distinguish primary initiator-derived radicals from radicals produced by successive decarboxylation, the latter ones are denoted by lower case characters and the former ones by capitals.

For mass analysis via ESI-MS, polymer molecular masses should be below 2000 amu, in which limitation is set by the ion trap mass analyzer. To produce such low molecular weight material, the MMA polymerizations were performed at relatively high diacyl peroxide concentrations, typically of $0.1\ mol\ L^{-1}$, in solution of benzene. The high initiator concentrations make radical termination, by combination or by disproportionation, the dominant polymer formation processes. In case of disproportionation, the produced macromolecules contain either an **X** or a **y** moiety as the end group, whereas termination by combination yields macromolecules with two
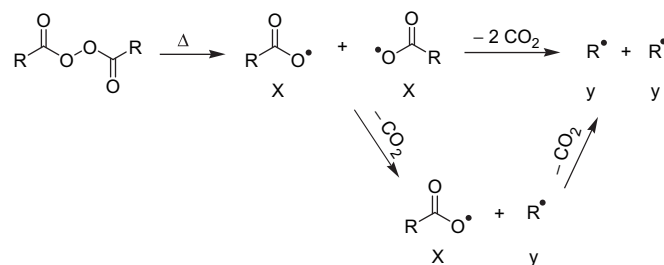
Scheme 1. Decomposition of symmetric diacyl peroxides.

such end groups. The low chain-transfer activity of benzene avoids the occurrence of significant amounts of solvent-derived end groups [29]. MMA polymerizations in toluene solution, for example, may yield large fractions of benzyl moieties as end groups [10]. Benzyl end groups have been observed by Hatada et al. [30] in ^1H NMR spectroscopic studies into the end groups produced in DBPO-initiated MMA polymerizations in toluene solution at 100 °C. These authors reported an approximate ratio of 1:2.5 between benzoyloxy and phenyl end groups. To the best of our knowledge, the present study is the first one to measure the end-group characteristics for a range of diacyl peroxides including alkyl and aryl components.

2. Experimental

2.1. Polymer synthesis

Diacyl peroxides (AKZO Nobel) and benzene (99.7%, Merck; caution – carcinogen, handle with care) were used as received. Methyl methacrylate (99.0%, Fluka) was purified via distillation under reduced pressure and was deoxygenized by purging with nitrogen. Methyl methacrylate–benzene mixtures, 1:2 v/v, containing $0.1\ mol\ L^{-1}$ diacyl peroxide were reacted for about 12 min in a thermostated block heater at 95 °C, with the exception of the polymerizations initiated by DIBP, where peroxide concentration and reaction temperature were $0.2\ mol\ L^{-1}$ and 80 °C, respectively. Monomer conversion typically exceeded 50%. The polymeric material was isolated by evaporating residual monomer and benzene.

2.2. Mass analysis via ESI quadrupole ion trap

The ESI-MS experiments were carried out using a Finnigan LCQ ion trap mass spectrometer (Thermo Finnigan, San Jose, CA, USA) equipped with an atmospheric pressure ionization source operated in the nebulizer-assisted electrospray mode. Calibration within the mass range 195–1822 amu was carried out with caffeine, MRFA (L-methionyl-arginylphenylalanyl-alanine acetate H₂O), and Ultramark© 1621 with all these materials being purchased from Aldrich. The spectra were obtained in the positive ion mode within the *m/z* range 100–2000 at a spray voltage of 4.5 kV and a capillary temperature of 200 °C. Nitrogen was used as sheath gas (flow: 30 units) and He as the bath gas. The polymer samples were dissolved
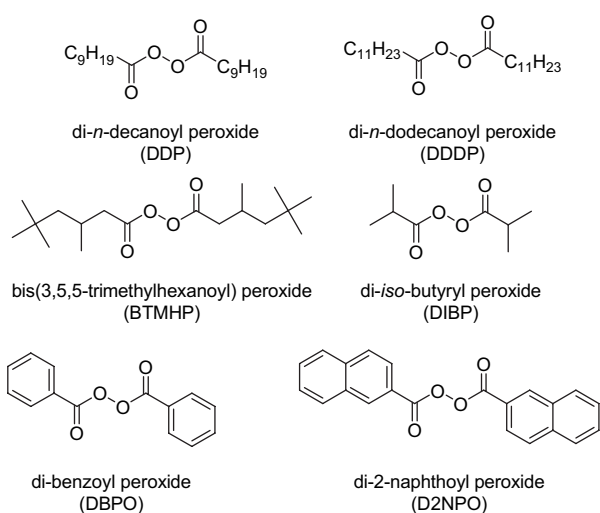
Chart 1. Symmetric diacyl peroxides used in the present study.

in a 3:1 v/v CH_2Cl_2–methanol mixture at a concentration of about 100 μg mL^{-1}. The samples were introduced into the electrospray interface by injection via a syringe pump of 3–5 μL min^{-1} within 2 min. The ESI-MS spectra presented below result from co-addition of about 200 individual spectral traces. Repeatability of the measured mass over charge values was excellent. Relative peak intensities were found to be reproducible within ±5%.

2.3. Mass analysis via ESI-FT-ICR

The polymeric samples were dissolved in a CH_2Cl_2–methanol (1:1, v/v) mixture containing 5 mM ammonium acetate. Tuning solution (Agilent) was added as an internal calibration standard. The solutions were introduced via a syringe pump (74900, Cole Parmer, USA) at a flow rate of 2 μL min^{-1}. The high-resolution ESI-MS measurements were performed on a 7 Tesla APEX IV FTICR MS instrument (Bruker Daltonics, Billerica, USA) equipped with an APOLLO electrospray ion source. An electrospray voltage of 4.2 kV, a capillary exit voltage of 100 V, and a nebulizing gas pressure of 30 psi nitrogen were applied to generate the spray. The temperature of the drying gas (nitrogen) was set to 300 °C. Ions were accumulated in the hexapole region for 0.05–0.3 s before being transferred into the ICR cell. They were measured via broadband excitation in the m/z range from 200 to 1700.

3. Results and discussion

Shown in Fig. 1a is the ESI-MS spectrum of a poly(MMA) sample obtained by polymerization in benzene solution at 95 °C using di-n-decanoyl peroxide (DDP) at an initial content of 0.1 mol L^{-1} as the initiator. The pattern of spectral positions is repetitive with the mass of one MMA segment, 100.05 amu, being the repeat unit. Depicted in Fig. 1b is the m/z range from 940 to 1040, which covers the range of one MMA repeat unit in the region of maximum intensity of the spectrum in Fig. 1a. The three major ESI-MS components in Fig. 1b may be unambiguously assigned to two components produced by radical termination via disproportionation, at m/z 949.7 and 951.7, and to a species resulting from radical combination, at m/z 977.6. More precisely, the components at m/z 949.7 and 951.7 characterize molecules that are ionized by a sodium ion and that are composed of eight MMA repeat units and one nonyl unit, reflecting the end group produced by decarboxylation of the nonyl carbonyloxy primary radical from initiator decomposition. Because of transfer of a hydrogen atom during disproportionation, the two components differ in m/z by +1 and −1 from the value given by the sum of masses of eight MMA repeat units, one nonyl moiety, and one sodium ion, which is 950.7. The ion at m/z 977.6 is due to an oligomer species consisting of seven MMA repeat units, two nonyl units and one sodium ion. Additionally, ^{13}C isotope ions are clearly separated for all compounds.

The weak spectral component at m/z 1009.3 is assumed to be an oligomeric product from combination of two radicals, each containing a nonyl group, with an oxygen (O_2) unit being
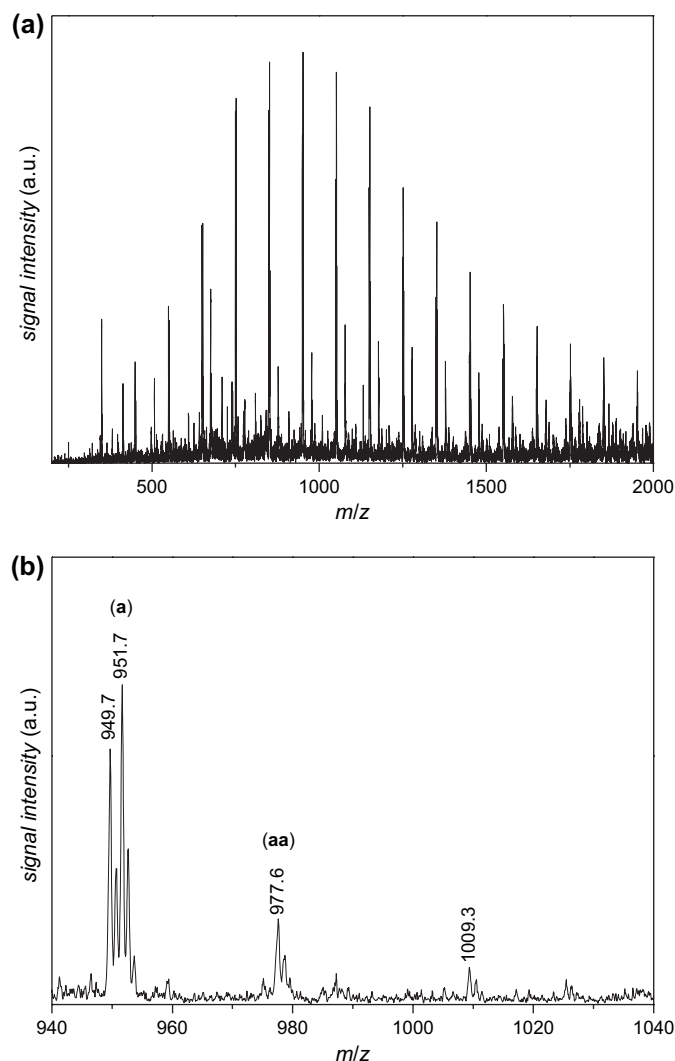

Fig. 1. ESI-MS spectrum of a poly(MMA) sample obtained by polymerization in benzene solution at 95 °C using di-n-decanoyl peroxide (DDP) as the initiator: (a) full mass range under investigation; (b) zoom into the m/z range of one MMA monomer repeat unit.

incorporated into one of the radicals. Such components are known to occur in the early polymerization period as a consequence of imperfect de-oxygenation [31,32]. Furthermore, there are a few very weak components in Fig. 1b. None of them is indicative of any n-nonyl carbonyloxy moiety contained as an end group. Disproportionation and combination components of species with n-nonyl carbonyloxy end groups would give signals at m/z 993.5/995.5 and 965.6, respectively. Polymeric material with both n-nonyl carbonyloxy and a n-nonyl moiety being the end groups would give rise to a signal at m/z 1021.6. The absence of a signal at any of these m/z values indicates that the n-nonyl carbonyloxy radical is rather short lived and undergoes decarboxylation prior to adding to an MMA molecule. Thus primary fragments of initiator decomposition, denoted by capital characters (see Scheme 1), contribute neither to starting chain growth nor to terminating growing chains. The nonyl moiety **a** is the only detectable polymeric end group. The components in Fig. 1b are referred

to as (**a**) and (**aa**), indicating the end groups and the mode of termination, i.e., disproportionation and combination, respectively. In Table 1, the measured m/z values of the disproportionation and combination peaks are listed together with the associated theoretical values calculated from the atomic masses.

The poly(MMA) samples prepared with di-*n*-dodecanoyl peroxide (DDDP) as the initiator exhibit the same type of behavior as seen with DDP. Three pronounced ESI-MS signals occur in the mass range of one MMA repeat unit. The pair of components in the mass range of 1000–1100 (Fig. 2), at m/z 1077.7 and 1079.7, is assigned to polymeric products from disproportionation, each containing one undecyl end group **b**. The third component, (**bb**), at m/z 1033.6, is due to an oligomeric MMA species containing two undecyl moieties, which is produced by combination of two radicals. The measured and calculated m/z values are listed in Table 1. The weak signal at m/z 1065.4 is assigned to an oligomeric species from combination (**bb**) including one oxygen (O_2) unit. As with DDP-initiated MMA polymerizations, the ESI-MS spectrum of poly(MMA) from DDDP-induced polymerization provides no indication of primary fragments from DDDP decomposition occurring as end groups.

ESI-MS data measured on poly(MMA) samples produced by initiation with bis(3,5,5-trimethylhexanoyl)peroxide (BTMHP) at 95 °C are shown in Fig. 3. Also with this diacyl peroxide, a pair of disproportionation peaks (together with the satellite bands resulting from ^{13}C isotope ions) is seen at m/z values of 935.7 and 937.8. Each of these two components contains one 2,4,4-trimethylpentyl end group, **c**. The signal at m/z 949.6 is due to MMA oligomers produced by termination via combination. These molecules contain two 2,4,4-trimethylpentyl end groups. They are referred to as component (**cc**). The measured and calculated m/z values are listed in Table 1. As with DDP and DDDP, no indication is seen of end groups which contain an alkyl carbonyloxy moiety. This observation also suggests that the primary 2,4,4-trimethylhexanoyloxy radical is not undergoing a 1,5-hydrogen shift reaction prior to decarboxylation. This reaction would yield a relatively stable carbon-centered radical which should show up as an end group. The very weak component at m/z 981.5 is due to molecules which contain seven MMA units, two 2,4,4-trimethylpentyl moieties and one O–O unit.
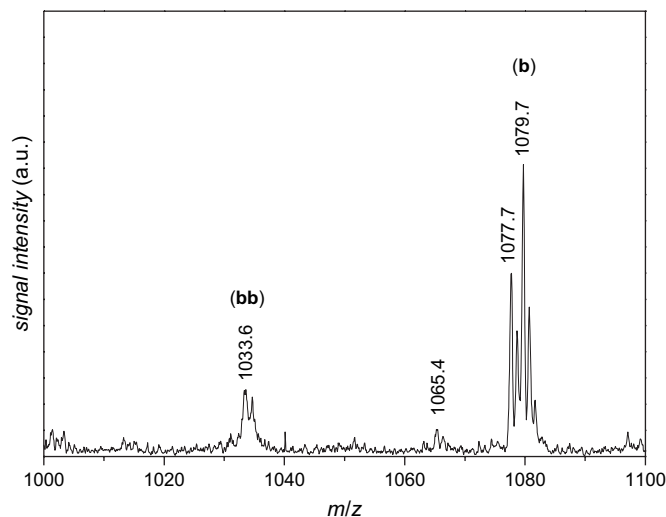

Fig. 2. ESI-MS spectrum of a poly(MMA) sample obtained by polymerization in benzene solution at 95 °C using di-*n*-dodecanoyl peroxide (DDDP) as the initiator. An m/z range corresponding to a single MMA repeat unit is shown.

Upon decarboxylation, the alkyl carbonyloxy radicals from decomposition of DDP, DDDP, and BTHMP yield primary carbon-centered radicals, $RCH_2^\bullet$. Although these primary alkyl radicals are high in energy, the decarboxylation step is sufficiently fast to occur before the intermediate alkyl carbonyloxy radical adds to an MMA molecule. Decarboxylation of alkyl carbonyloxy radicals, which yields species with the radical functionality at secondary or tertiary carbon atoms, should be even faster. Thus it comes as no surprise that the ESI-MS data measured on products from MMA polymerization initiated by di-*iso*-butyryl peroxide (DIBP) provide no indication of *iso*-propyl carbonyloxy end groups (Fig. 4). The major signals in Fig. 4 are assigned to the disproportionation twin peaks (**d**) and to the species (**dd**) reflecting termination by combination. The signal positions are listed in Table 1. The weak signal at m/z 1004.3 may be assigned to an MMA nonamer carrying two propyl end groups, but having been ionized by NH_4^+, which ion is present in trace amounts. The relative intensities of the components (**dd**) and (**d**) (with an attached sodium ion) suggest that a component (**d**) with ionization by ammonium will not be easily detectable because of too low intensity.

Table 1
Detailed peak assignments of the ESI-MS spectra of poly(MMA), initiated by alkyl diacyl peroxides in benzene

Initiator	Peak	End group		$(m/z)^{theo}$	$(m/z)^{exp}$
DDP	**a**	*n*-Nonyl	–	949.6/951.6	949.7/951.7
	aa	*n*-Nonyl	*n*-Nonyl	977.7	977.6
DDDP	**b**	*n*-Undecyl	–	1077.6/1079.6	1077.7/1079.7
	bb	*n*-Undecyl	*n*-Undecyl	1033.7	1033.6
BTMHP	**c**	2,4,4-Trimethylpentyl	–	935.5/937.5	935.7/837.8
	cc	2,4,4-Trimethylpentyl	2,4,4-Trimethylpentyl	949.6	949.6
DIBP	**d**	2-Propyl	–	1065.6/1067.6	1065.5/1067.5
	dd	2-Propyl	2-Propyl	1009.6	1009.4

For disproportionation peaks with only one end group the value pair of the two occurring peaks is reported.
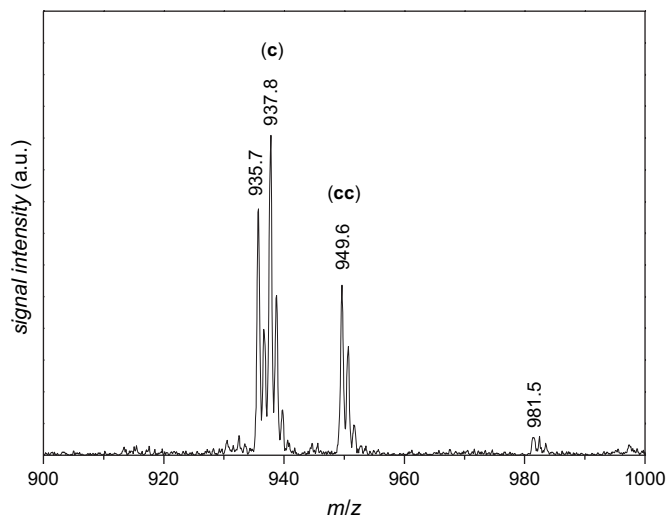
Fig. 3. ESI-MS spectrum of a poly(MMA) sample obtained by polymerization in benzene solution at 95 °C using bis(3,5,5-trimethylhexanoyl) peroxide (BTMHP) as the initiator. An *m/z* range corresponding to a single MMA repeat unit is shown.

Despite the close similarity of the end-group characteristics of the four diacyl peroxides, DDP, DDDP, BTMHP, and DIBP, also a difference needs to be noted in comparing Figs. 1–4. The intensities of the ESI-MS peaks reflecting termination by combination are below the intensities of the associated peaks for species from termination by disproportionation in case of DDP, DDDP, and BTMHP, whereas the reverse is true for the ESI-MS spectra of the samples from DIBP-induced MMA polymerization. This observation appears to be surprising in view of the fact that the ratio of termination by disproportionation to termination by combination should be primarily determined by monomer characteristics and thus should be approximately the same with all four diacyl peroxides. The sample from DIBP-induced MMA polymerization

(see Fig. 4) differs from the ones obtained with DDP, DDDP, and BTMHP acting as the initiator in that the radical concentration during polymerization was significantly higher. The reason behind this higher radical concentration is that the decomposition rate coefficient of DIBP, even at the lower temperature of 80 °C, is by about a factor of 20 above the one of DDP, DDDP, and BTMHP at 95 °C. The higher rate is due to decarboxylation yielding a secondary carbon-centered radical, which makes this reaction occur almost instantaneously after scission of the peroxy bond and which provides an additional driving force for DIBP decomposition.

As will be illustrated in a forthcoming study [33], the ratio of disproportionation to combination peaks observed at a given polymer size, e.g., within the same repeat unit, is largely affected by radical concentration, although the ratio of disproportionation to combination rate coefficients by itself stays constant. For measuring the ratio of these two rate coefficients it is mandatory to take the full molecular weight distribution (MWD) into account. Information about the full MWD may be obtained via the evaluation of ESI-MS data covering extended mass ranges, e.g., as the one depicted in Fig. 1a. Contained in such kinetic analysis will be the fact that peaks associated with disproportionation dominate at lower polymer weights whereas peaks reflecting combination products dominate at higher molecular weights. This latter point, which rules out the possibility of simply reading the ratio of disproportionation to combination rate coefficients from ESI-MS signal intensities at any given degree of polymerization, will also be addressed in the forthcoming study [33]. In the present paper, the primary focus will be on ESI-MS peak positions, hence, on speciation. Signal intensities and thus concentrations will not be addressed in depth.

Shown in Fig. 5 is the ESI-MS spectrum of a sample from MMA polymerization in benzene solution with di-benzoyl peroxide (DBPO) [34] acting as the initiator. The data reveal that two types of radicals are involved in starting chain growth.
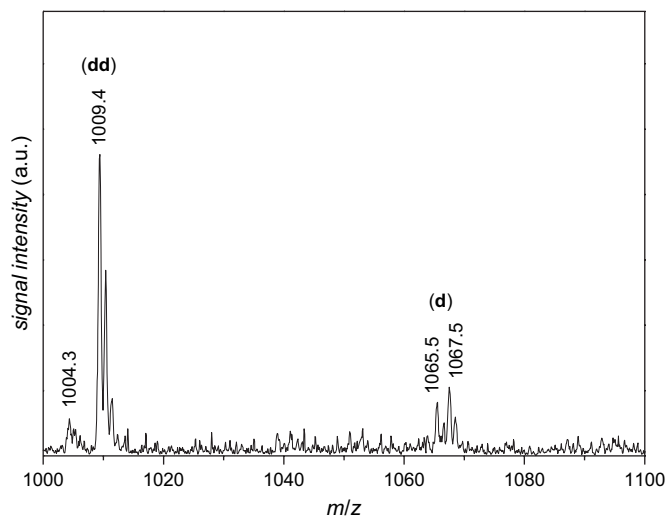

Fig. 4. ESI-MS spectrum of a poly(MMA) sample obtained by polymerization in benzene solution at 80 °C using di-*iso*-butyryl peroxide (DIBP) as the initiator. An *m/z* range corresponding to a single MMA repeat unit is shown.
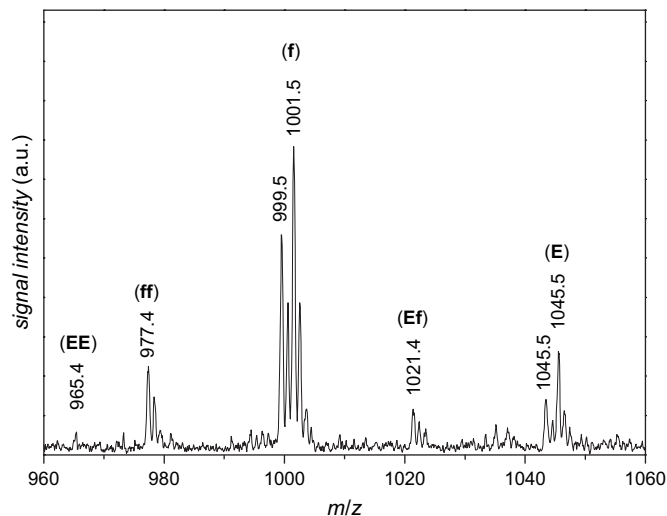

Fig. 5. ESI-MS spectrum of a poly(MMA) sample obtained by polymerization in benzene solution at 95 °C using di-benzoyl peroxide (DBPO) as the initiator. An *m/z* range corresponding to a single MMA repeat unit is shown.

Table 2
Detailed peak assignments of the ESI-MS spectra of poly(MMA), initiated by aromatic diacyl peroxides in benzene

Initiator	Peak	End group		$(m/z)^{theo}$	$(m/z)^{exp}$
DBPO	**f**	Phenyl	−	999.5/1001.5	999.5/1001.5
	ff	Phenyl	Phenyl	977.5	977.4
	E	Benzoyloxy	−	1043.4/1045.4	1043.5/1045.5
	EE	Benzoyloxy	Benzoyloxy	965.4	965.4
	Ef	Phenyl	Benzoyloxy	1021.4	1021.4
D2NPO	**h**	Naphthyl	−	1049.5/1051.5	1049.5/1051.5
	hh	Naphthyl	Naphthyl	1077.5	1077.3
	G	Naphthoyloxy	−	1093.5/1095.5	1093.5/1095.5
	GG	Naphthoyloxy	Naphthoyloxy	1065.4	1065.3
	Gh	Naphthyl	Naphthoyloxy	1121.5	1121.3

For disproportionation peaks with only one end group the value pair of the two occurring peaks is reported.
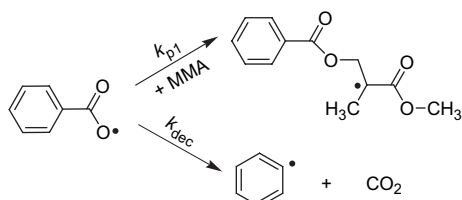
Both the primary decomposition fragments, i.e., the benzoyloxy radical **E** and the phenyl radical **f**, which result from decarboxylation of **E**, are seen as end groups. In addition to the two disproportionation components, (**E**) and (**f**), the three combination peaks that are expected to occur in systems with two different end groups, (**EE**), (**Ef**), and (**ff**), are found. The peak assignments are given in Table 2.

It has been reported that phenyl radicals produced from benzoyloxy radicals may abstract hydrogen atoms at elevated temperatures [35]. If this reaction occurs with a monomer molecule, a monomer radical would be produced that might become a polymeric end group. The absence of polymer without initiator-derived end groups at m/z 923.4 indicates that such transfer steps of phenyl radicals play no significant role in the systems studied here.

Quantitative analyses via ESI-MS are not straightforward [36]. Relative amounts of the different types of end groups may be tentatively estimated from the ratio of signal intensities of the two types of disproportionation peaks, i.e., of (**E**) to (**f**) in Fig. 5. The signal intensities of (**E**) and (**f**) were determined by integration. Assuming identical ESI-MS sensitivity of the (**E**) and (**f**) species, the data in Fig. 5 suggest that the two species occur at a ratio of about 1:3. Thus 75% of the primary phenyl carbonyloxy radicals decarboxylate in the time span between peroxide decomposition and initiation of chain growth. The probability that two MMA radicals with identical end group react with each other should scale with the square of the associated radical concentrations. From (**E**):(**f**) = 1:3, the ratio of intensities of the combination peaks (**EE**):(**ff**) is thus predicted to be 1:9. The experimentally observed ratio of integrated component intensities is (**EE**):(**ff**) = 1:8.3, which is remarkably close to the prediction. ESI-MS signal intensities thus appear to scale with the concentration of the associated

species to a good approximation. That the concentration of MMA oligomer species with phenyl end groups is approximately three times above the one of MMA radicals with carbonyloxy end groups is consistent with NMR evidence on polymer from DBPO-initiated MMA polymerization at 100 °C by Hatada et al. [30]. Within this earlier study, however, the phenyl carbonyloxy end groups were not directly measured. Their concentration was inferred from the one of benzyl end groups, which were assumed to be produced by quantitative chain-transfer reaction of the primary oxygen-centered phenyl carbonyloxy radicals to the solvent toluene.

The ratio of **E** to **f** end groups may also be roughly estimated via the quantum chemically derived rate coefficient for decarboxylation of the **E** radical, k_{dec}, and the reported rate coefficient for addition of a methyl radical to an MMA molecule, k_{p1}. The ratio of (**E**):(**f**) intensities should be given by $k_{p1} \times c_{MMA} \times c_E / k_{dec} \times c_E = k_{p1} \times c_{MMA} / k_{dec}$ (see Scheme 2). The k_{p1} value for 26.85 °C reported by Fischer and Radom [37] is 4.9×10^5 L mol^{-1} s^{-1}. Via the associated logarithmic frequency factor, $\log(A/\text{L mol}^{-1}\text{s}^{-1}) = 8.9$, k_{p1} for 95 °C is calculated to be 2.0×10^6 L mol^{-1} s^{-1}. For $c_{MMA} = 4$ mol L^{-1},
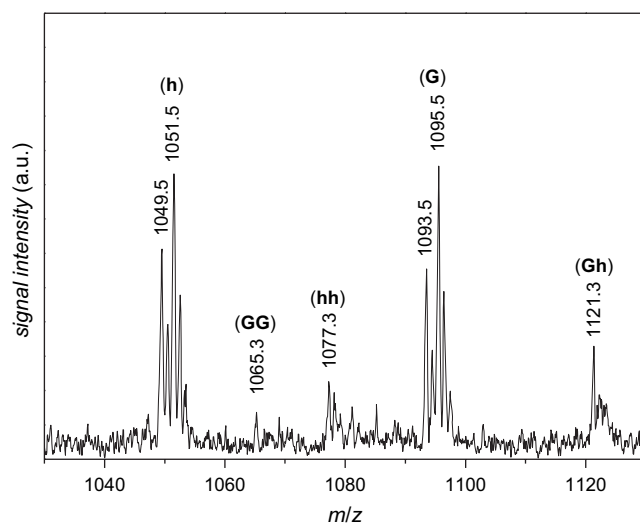
Fig. 6. ESI-MS spectrum of a poly(MMA) sample obtained by polymerization in benzene solution at 95 °C using di-2-naphthoyl peroxide (D2NPO) as the initiator. An m/z range corresponding to a single MMA repeat unit is shown.
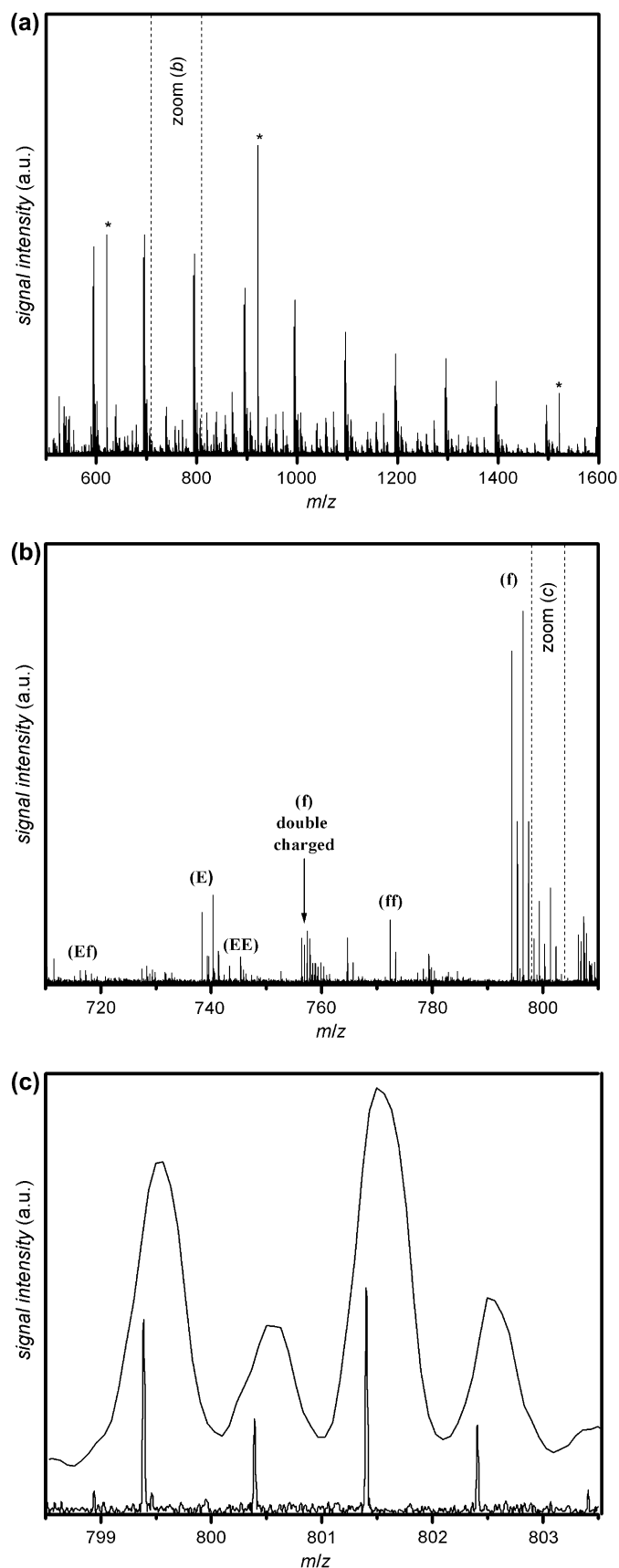
Scheme 2. Competing reactions of the phenyl carbonyloxy radical.

which is the monomer concentration used in our experiments, $k_{p1} \times c_{MMA}$ at 95 °C is estimated to be $8.0 \times 10^6 \, s^{-1}$. For k_{dec}, the following set of Arrhenius parameters has been reported by Chateauneuf et al. [38]: $\log(A/s^{-1}) = 12.6$ and $E_A = 35.9 \, kJ \, mol^{-1}$, which yields $k_{dec}(95 \, °C) = 3.1 \times 10^7 \, s^{-1}$. The resulting number for $k_{p1} \times c_{MMA}/k_{dec}$ thus is 1:3.9 which, in view of the fact that the quantum-chemical calculations were carried out for the addition of a methyl rather than a benzoyloxy radical to MMA and without taking the dense solvent environment into account, is remarkably close to the experimentally measured (**E**):(**f**) peak intensity ratio of 1:3.

As a second aromatic diacyl peroxide, di-2-naphthoyl peroxide (D2NPO) has been used to initiate MMA polymerization in benzene solution at 95 °C. The ESI-MS spectrum of poly(MMA) from D2NPO-induced MMA polymerization (Fig. 6) is indicative of chain growth having been started by two types of end groups, the 2-naphthyl carbonyloxy radical **G** and by the 2-naphthyl radical **h**. Under the assumption that the relative signal intensities of the disproportionation peaks, (**G**) and (**h**), reflect the content of the two types of polymeric end groups, the data in Fig. 6 indicate that radicals of types **G** and **h** are starting chain growth to approximately the same extent. The enhanced fraction of naphthyl carbonyloxy as compared to phenyl carbonyloxy end groups (see Fig. 5) is assigned to a lower decarboxylation rate coefficient of naphthyl carbonyloxy radicals because of the more extended aromatic system. This trend is also indicated by quantum-chemical DFT calculations of decarboxylation rate coefficients of phenyl carbonyloxy and naphthyl carbonyloxy radicals [24–28].

The ESI-MS signal-to-noise ratio in the experiments with the aromatic diacyl peroxides (Figs. 5 and 6) is lower in comparison with the studies of poly(MMA) from initiation with alkyl diacyl peroxides (Figs. 1–4), which may be due to the fact that aromatic systems are poorly ionized in soft ionization mass spectrometry. In view of the reduced signal intensity with the aromatic diacyl peroxides it may be argued that additional ESI-MS components are hidden behind the broadened noisy bands. In order to demonstrate that only a very few components are contributing to the relatively broad band contour occurring in ion trap ESI-MS and to probe the reliability of the respective m/z values obtained from such peaks, high-resolution FT-ICR-MS experiments have been carried out for polymeric material initiated by DBPO as an example.

3.1. ESI-FT-ICR mass spectrometry

In conventional ion trap MS, the maximum mass resolution of about 2000 together with the dispersion of individual peaks prevent the detection of individual signals which differ in m/z by less than 0.5 amu. The actual number of separate components may be accessed by highly mass-resolved electrospray

Fig. 7. ESI-FT-ICR mass spectrum of a poly(MMA) sample obtained by polymerization in benzene solution at 95 °C using di-benzoyl peroxide (DBPO) as the initiator. (a) Extended spectrum (peaks due to the calibration standards are marked by an asterisk), (b) zoom into an m/z range covering one monomer repeat unit, (c) comparison between the ESI-ion trap and the ESI-FT-ICR mass spectra for one disproportionation component (**f**).

Table 3
Detailed peak assignment of the ESI-FT-ICR mass spectrum of poly(MMA), initiated by di-benzoyl peroxide (DBPO) in benzene solution for the *m/z* range from 710 to 810

Peak	End group		Elemental composition	$(m/z)^{theo}$	$(m/z)^{exp}$	Deviation[a]/ppm
f₁	Phenyl	− (−H)	$C_{41}H_{60}O_{14} + NH_4^+$	794.4321322	794.4319830	0.19
f₂	Phenyl	− (+H)	$C_{41}H_{62}O_{14} + NH_4^+$	796.4477823	796.4482160	0.54
Ff	Phenyl	Phenyl	$C_{42}H_{58}O_{12} + NH_4^+$	772.4266529	772.4269080	0.33
E₁	Benzoyloxy	− (−H)	$C_{37}H_{52}O_{14} + NH_4^+$	738.3695319	738.3695319	0.13
E₂	Benzoyloxy	− (+H)	$C_{37}H_{54}O_{14} + NH_4^+$	740.3851820	740.3849747	0.28
EE	Benzoyloxy	Benzoyloxy	$C_{39}H_{50}O_{14} + H^+$	743.3273328	743.3266489	0.92
Ef	Phenyl	Benzoyloxy	$C_{38}H_{50}O_{12} + NH_4^+$	716.3640526	716.3642350	0.25

[a] Deviations were calculated as: $((m/z)^{theo} − (m/z)^{exp})/(m/z)^{theo}$.

ionization Fourier transform ion cyclotron resonance (ESI-FT-ICR) mass spectrometry. Such spectra taken for oligomeric species from DBPO-initiated MMA polymerization are shown in Fig. 7. The extended *m/z* range in Fig. 7a covers singly ionized polymeric species over 11 MMA repeat units as well as twofold and multiply charged species occurring at low *m/z* values. The singly charged mass spectrum displays a shape as is commonly observed with synthetic polymers. The intense peak at *m/z* 922 is due to the calibration standard (peaks due to the calibration standards are marked by an asterisk). The overall band shape is not directly correlated to the actual chain-length distribution of the oligomeric species, as mass discrimination effects occur that depend on the ionization technique and on other parameters of the experimental set-up. Especially at lower molecular weights, the ionization sensitivity may be strongly affected by oligomer size.

Zooming into the mass range of one repeat unit (Fig. 7b) demonstrates the significantly enhanced mass resolution of ESI-FT-ICR. The spectral information deduced from ion trap ESI-MS (see Fig. 5) is contained in the ESI-FT-ICR mass spectrum with, however, several additional peaks being present. They arise from ionization by ammonium and by proton attachment, but are also due to doubly charged species, which are easily identified by an isotopic peak difference of 0.5 Da and by a separation of successive repeat units by just half the mass of one MMA unit. The enormous potential of ESI-FT-ICR mass spectrometry becomes very clear by zooming into the mass range covering one group of signals, e.g., the (**f**) component. The significant improvement in mass resolution is illustrated in Fig. 7c by superimposing the mass spectra obtained from ESI-FT-ICR mass spectrometry with the one from ion trap ESI-MS. The slight shift in the peak maximum positions indicates the instrumental limitations of the ion trap ESI-MS. The *m/z* values from ESI-FT-ICR are accurate within ±1 ppm (see Table 3), whereby the elemental compositions of the polymeric chains are unambiguously verified. The four individual peaks in Fig. 7c are solely due to the disproportionation pair, separated by 2 amu, with each of these two bands being accompanied by an isotopic satellite containing one or more ^{13}C atom. The high-resolution spectrum clearly demonstrates that no additional *m/z* components occur beneath the broadened signals seen in the ion trap ESI-MS spectrum. The preceding analysis, which has been exclusively based on ion trap ESI-MS data, may thus be considered reliable.

4. Conclusions

End-group analysis by ESI-MS on poly(methyl methacrylates) from free-radical polymerization using different types of diacyl peroxides, R−(CO)O−O(CO)−R, as the initiator reveals clear differences between the cases in which the R moiety is an alkyl group or an aryl group. With alkyl diacyl peroxides only the alkyl R moiety is observed as an end group. Only one such end group occurs in the case of termination by disproportionation and two such end groups are seen if termination takes place by combination. With aryl diacyl peroxides, such as dibenzoyl peroxide or di-naphthoyl peroxide, both the aryl moiety and the aryl carbonyloxy moieties, R and R−(CO)O, are found as end groups. Thus five ESI-MS components are seen in the spectral range associated with each monomer repeat unit (or seven components if one counts the disproportion twin peaks as two separate components). They result from termination both by disproportionation and by combination of two types of radicals which differ in their terminal unit, that is, in the species that has started their growth. That part of the primary R−(CO)O• radicals from peroxide decomposition are capable of initiating chain growth (at the polymerization temperature of 95 °C) relates to aromatic delocalization which enhances the stability toward decarboxylation of these radicals. Additional ESI-FT-ICR mass spectrometry experiments indicate that the end-group analysis based on ion trap ESI-MS is sufficient to identify the end-group characteristics of the polymer samples prepared in the present study and confirm the elemental composition of the detected species.

discussions with Professor G.T. Russell on the mode of termination in free-radical polymerization.

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