Mapping Free Radical Reactivity: A High-Resolution Electrospray Ionization−Mass Spectrometry Study of Photoinitiation Processes in Methyl Methacrylate Free Radical Polymerization

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ABSTRACT: High-resolution electrospray ionization−mass spectrometry (ESI-MS) was applied to study the polymeric product spectrum generated by the pulsed laser polymerization (PLP) of methyl methacrylate (MMA) at temperatures ≤0 °C in the presence of the photoinitiators 2,2-dimethoxy-2-phenylacetophenone (DMPA), benzoin, benzil, benzoin ethyl ether (BEE), and 2,2-azobisisobutylnitrile (AIBN). Termination products, both combination and disproportionation, were identified with high accuracy. Both the benzoyl and acetal fragments generated as a result of DMPA photocleavage were found to initiate and highly likely terminate polymerization. Under the conditions studied, the acetal radical produced upon DMPA photolysis fragments further to yield methyl radicals which seem to act predominantly as terminating moieties. Both the benzoyl and ether fragments produced as a result of benzoin photocleavage were found to act as initiating and probable terminating species, indicating that the ether radical fragment does not act exclusively as a terminating species. Additionally, increasing laser intensity and/or irradiation repetition rate (i.e., energy deposition into the system) results in more complex product distributions of the MMA polymers produced via photoinitiation (with the exception of AIBN). Temperature was determined to have a minor influence on the resulting product distribution under the conditions examined.

Introduction

Photopolymerizations constitute an important avenue for the preparation of synthetic polymers in both industry and academia. Photopolymerization can be achieved through the use of photoinitiators (PIs), photo-cross-linkable polymers, and photo-cross-linking agents.[1] PIs are used for the polymerization of functional monomers, oligomers, and polymers[2] for use in applications including UV-curing of coatings and inks as well as for more specialized applications such as dental restorative materials[3,4] and biomaterials.[5,6] The present study focuses on the free radical photopolymerization of methyl methacrylate (MMA) using various PIs employed frequently in UV-curing applications, photoimaging, and kinetic studies (see for example refs 7−10).

MMA was selected as the monomer for several reasons. First, all necessary kinetic parameters of the monomer are known (see Table S1 of the Supporting Information). Furthermore, MMA has been extensively studied with regard to its mechanistic pathway including propagation,[11] termination,[12] and chain transfer reactions.[13,14] Importantly, polyMMA is the basis of many material families including Perspex, Plexiglas, and Lucite, which have a wide range of applications.

The diverse and widespread use of alkyl methacrylate polymers stems from their many advantageous material properties. For example, the pure aliphatic structure of the methacrylate backbone and effective steric hindrance of the polymer chains results in alkyl methacrylate polymers exhibiting excellent weather resistance characteristics. Additionally, poly(alkyl methacrylate)s are characterized by a lack of oxidative degradation or ester hydrolysis. However, a disadvantageous property of these polymers is that they are susceptible to UV and thermal degradation (see for example refs 15−19). The thermal degradation of MMA is understood to involve the initiation of depropagation with first-order termination or depropagation by chain end and random chain scission and subsequent unzipping of the polymer chain.[20] The type of end group on the polymer is dictated by the experimental conditions, route, and mechanism of polymer synthesis; however, there is limited information as to the polymer chain ends produced through photopolymerization, thus hindering our ability to design better photopolymeric materials with improved resistance to harsh environmental conditions.

Ideally, synthesis of a polymeric structure that is completely characterized with respect to molecular weight (number- and weight-average as well as stereoregularity) and has end groups that withstand degradation would improve the longevity of poly(alkyl methacrylate)s produced via photopolymerization. The introduction of a saturated end group with high bond energy at the polymer chain end has been postulated to reduce end initiation effects and raise the thermal degradation temperature of polyMMA.[20] An improved understanding of the photolysis products obtained from several PIs subjected to various initiation conditions, and the subsequent photolysis product reactivity toward the alkyl methacrylate, would enhance greatly our ability to tailor photopolymer properties for specific applications. In this present study, the mechanistic details of the photoinitiation process are investigated with particular emphasis on the ability of the primary and secondary photoinitiator derived radical fragments to initiate and terminate macromolecular growth.

Aromatic ketones are the most versatile photoinitiators in commercial practice as their absorptions occur at longer wavelengths and their quantum yields are higher than aliphatic ketones.[21] Ketones undergo homolysis (often simultaneously) via either one of two processes: fragmentation or hydrogen abstraction.[21] The process of fragmentation is described in

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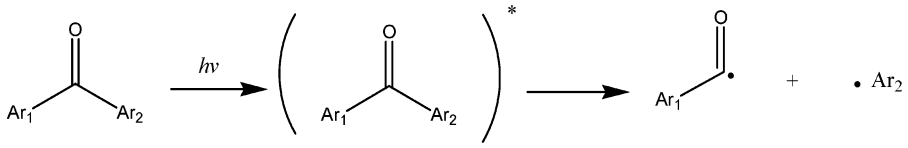
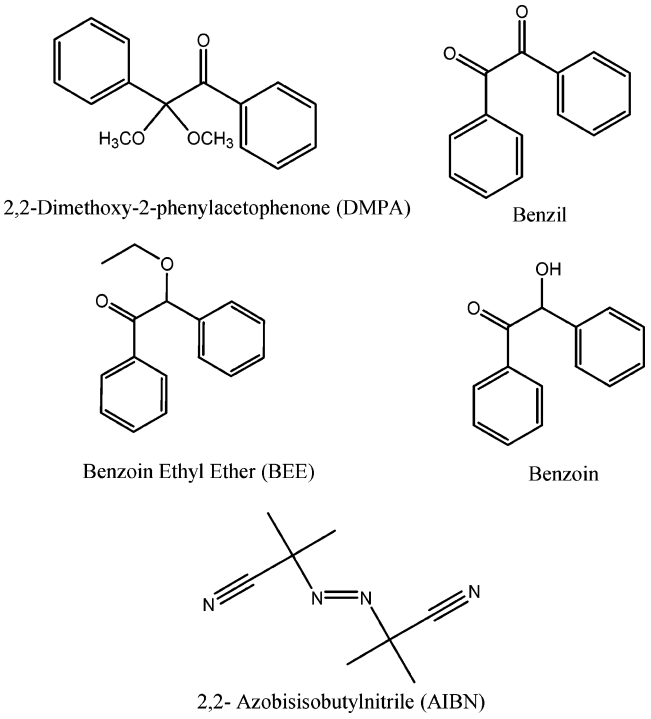
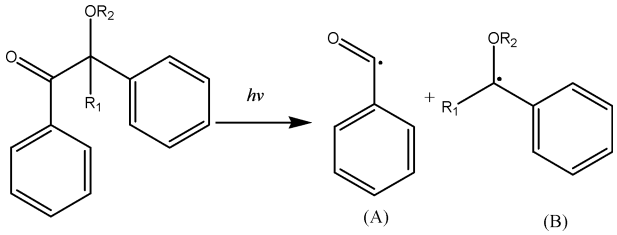
Scheme 1. Photolytic Pathway for Aromatic Ketone Photoinitiators[21]



Scheme 2. Photoinitiators Employed in the Present Study



Scheme 3. Benzoin Derivative Photocleavage[27]



Scheme 1. Hydrogen abstraction only occurs in the presence of a hydrogen donor (most commonly amines).[1]

The photoinitiators 2,2-dimethoxy-2-phenylacetophenone (DMPA), benzoin, benzoin ethyl ether (BEE), benzil, and 2,2-azobisisobutylnitrile (AIBN) were employed in this study (see Scheme 2) because they have been studied extensively with respect to their photodecomposition and excited-state products[22−24] and are common commercial photoinitiators often used in the presence of hydrogen donors. The relative amounts of fragmentation and hydrogen abstraction vary with the type of PI and hydrogen donor, as the stability of the free radicals formed in the photolysis may differ.[21] Since this study is aimed at examining free radical reactivities of PI photolysis products and hydrogen donors aid in the photocleavage of the PI, clouding true radical reactivity, no hydrogen donors were employed.

The PIs used (except AIBN; see Scheme 2) are all type I photoinitiators which undergo photochemical α-cleavage from the triplet state by a Norrish type I mechanism. AIBN is used commonly as both a thermal and photoinitiator.[25,26] Benzoin and BEE are used frequently as PIs for vinyl polymerizations due to their fast photochemical reaction.[1] Photochemical α-cleavage from the triplet state by a Norrish type I mechanism yields a benzoyl (A) and ether radical (B) (Scheme 3) and has been shown to be the main process for photolysis of benzoin and its derivatives in a wide temperature range.[1,27] A major drawback of benzoin ether PIs, however, is their low thermal stability and associated yellowing of cured coatings.[1]

There is uncertainty about the reactivity and role of the radical species (A) and (B) (Scheme 3). Pappas et al.[28,29] (using ^{14}C-labeled benzoin derivatives) found that for low radical and high monomer concentrations (MMA and methacrylate) the (A) and (B) radicals exhibit comparable efficiency and have the same reactivity. Hageman et al.[30] identify different reactivities and roles; however, benzoyl radicals are known to add efficiently to various unsaturated compounds.[1] Single pulse−pulsed laser polymerization (SP-PLP) experiments analyzed via matrix-assisted laser desorption and ionization−time of flight-mass spectrometry (MALDI-ToF-MS) have shown that for benzoin the benzoyl radical is the more reactive radical which may reduce the complexity of the resulting mass spectra.[31,32] Studies of various monomers with benzoin via SP-PLP by Kowollik[33] found a decrease in monomer conversion per single laser pulse with increasing photoinitiator concentrations. The reason for such behavior was attributed to an effective initiation of the benzoyl radical, while the ether radical was thought to be involved predominantly in termination events.

Benzil ketals, including DMPA, are another important class of PI. The efficiency of benzil ketals is considerably greater than that of benzoin ethers (i.e., benzoin and BEE).[1] Similar conjecture exists over the radical reactivity of the acetal fragment produced in DMPA photolysis.[34−36] Buback et al.[37] observed a decrease in monomer conversion per single laser pulse with increasing photoinitiator concentrations of DMPA in SP-PLP studies of various monomers. The reason for such behavior was attributed tentatively—similar to the arguments put forward in the case of benzoin and on the basis of kinetic observations alone—to the specific decomposition pathways and fragments of the photoinitiator. DMPA was postulated to decompose into both an inhibiting species (the acetal fragment) and an initiating species (the benzoyl fragment). A recent MALDI-ToF-MS investigation confirmed that the benzoyl fragment is indeed an effective initiator in MMA photopolymerization; however, the fate of the acetal fragment could not be ascertained due to the relatively poor resolution of the MALDI-ToF spectra.[38] While this study seeks to clarify the situation on the basis of an in-depth product analysis, it is important to note that the behavior of the radical species produced from the photocleavage of PIs may be temperature dependent. Thus, some care should be taken when extrapolating the experiments of the present study ($T \leq 0$ °C) to the higher temperatures (and pressures) of the SP-PLP experiments.

Despite numerous decomposition product studies over the past decades, the analysis of the photolytic products of these PIs as moieties in the polymer chain of poly(alkyl methacrylate) homopolymers, to the best of our knowledge, has yet to be studied in great detail. Limited terminal group analysis of photopolymerized products of 2-phenoxyethyl acrylate using MALDI-ToF-MS has been conducted by Kaji et al.[39] In the present study, the free redial reactivity of the photolysis products

of various commonly used PIs toward MMA is mapped in detail. Identifying possible products of all reaction pathways in a photoinitiated process requires highly sensitive experimental techniques; soft ionization mass spectrometry is a tool ideally suited for this task. The potential of mass spectrometric analysis for synthetic polymers has been discussed in numerous publications and review articles.[40−43] The two main mass spectrometry techniques suitable for the study of synthetic polymers are MALDI-ToF-MS[44,45] and ESI-MS.[46,47] The accessible mass range for MALDI-ToF-MS is significantly larger ($m/z \sim 100\,000$ amu) than for ESI-MS ($m/z \sim 4000$ amu); however, ESI-MS is a very soft ionization technique that allows the characterization of intact polymers.[48] ESI provides a molar response to oligomers, and fragmentation of oligomers does not occur under ESI conditions. Therefore, it is possible to obtain repeat unit and end group masses using ESI-MS.[48] Previously, the CAMD (Centre for Advanced Macromolecular Design) group has employed both MALDI-ToF-MS and ESI-MS to study mechanistic aspects of both conventional and living free radical polymerization[38,49−52] as well as to conduct fundamental kinetic investigations.[51]

The present study couples the pulsed laser polymerization (PLP) technique[54,55] with ESI-MS to carry out end group analysis of polymers formed using photoinitiation. The need to use the PLP technique in the synthesis of polyMMA stems from the molecular weight limitations associated with ESI-MS. PLP is an efficient and simple technique for obtaining desired molecular weights using photopolymerization, while allowing flexibility in initiator and monomer concentration. The principle behind PLP is that the molecular weight of the resulting polymer is controlled by the repetition rate of the incident light radiation under isothermal conditions. The propagation and average termination rate coefficients of free radical polymerizations are constant at isothermal conditions and low conversions.[27] The pulsing in PLP induces termination events at the time of the incident light irradiation; hence, when kinetic parameters are known, desired molecular weights can be targeted. In the case of UV curing, where the incident radiation is a constant source of (monochromatic) light there are no externally induced termination events. As a consequence, high molecular weight polymers are produced. Prior to the PLP experiments in this study, simulation work was undertaken using the program package PREDICI to find suitable PLP conditions under which molecular weight distributions for polyMMA below 4000 Da could be obtained. The parameters used in the PREDICI simulation are detailed in the Supporting Information (see Table S1).

By examining the end groups of photoinitiated polymers (synthesized under various conditions) using high-resolution ESI-MS, key information vital to improving the synthesis procedure and consequently the lifetime of UV-cured polymers can be obtained.

Experimental Section

Materials. Methyl methacrylate (MMA, Aldrich, 99%) and *n*-butyl methacrylate (*n*-BMA, Aldrich, 99%) were deinhibited by passing over basic alumina. 2,2-Dimethoxy-2-phenylacetophenone (DMPA) (Aldrich, 99%), benzil (Aldrich, 98%), and benzoin ethyl ether (BEE) (Aldrich, 99%) were used as received. Benzoin (Aldrich) and 2,2-azobisisobutylnitrile (AIBN) (DuPont) were recrystallized twice in ethanol prior to use. Photoinitiator purity was confirmed by ^{1}H NMR. Acetonitrile (Ajax, 99%) was used as received.

Polymerizations. All samples consisted of monomer (sample volume ~ 1.0 mL) with a photoinitiator concentration of 5×10^{-3}−1×10^{-2} mol L^{-1}. Prior to laser irradiation, all samples were deoxygenated with a nitrogen stream for a period of 12 min. Isothermal reaction conditions (from 0 to −26.2 °C) were maintained (by first allowing the sample to equilibrate for 10 min) using a recirculating bath including a feedback loop through a thermocouple attached to the side of the reaction cell. The reaction cell is a copper cell (120 × 120 × 70 mm) designed to hold a soda glass vial (75 × 12 mm). The bath fluid used was a 50:50 v/v mix of ethylene glycol and water. A Lamda Physik COMPex Pro 110 XeF pulsed laser system was used to generate radiation bursts (20 ns) with frequencies of 20 or 100 Hz for an overall polymerization time of 20 min at a wavelength of 351 nm with a single pulse energy ranging between 4 and 26 mJ. The laser beam was attenuated to 1 cm^2 using Thor Labs optics. Laser energy measurements were carried out with a Ophir AN/2 power meter. Care was taken to ensure a homogeneous intensity profile over the whole optical cross section. The applied laser pulse patterns were controlled with a handheld keypad. The resulting polymers were isolated by evaporating off the residual monomer. Cell design limited the study to atmospheric pressure. No stirring was applied.

Mass Analysis. ESI-MS experiments were carried out using a Thermo Finnigan LCQ Deca ion trap mass spectrometer (Thermo Finnigan, San Jose, CA). The ESI-MS is equipped with an atmospheric pressure ionization source which operates in the nebulizer-assisted electrospray mode. The instrument was calibrated with caffeine, MRFA, and Ultramark 1621 (all from Aldrich) in the mass range 195−1822 amu. All spectra were acquired in positive ion mode over the mass to charge range, m/z, 100−2000 with a spray voltage of 5 kV, a capillary voltage of 44 V, and a capillary temperature of 275 °C. Nitrogen was used as sheath gas (flow: 50% of maximum) while helium was used as auxiliary gas (flow: 5% of maximum). The eluent was a 6:4 v/v mixture of THF: methanol with an acetic acid concentration of 0.4 mM. Salt concentration has been shown to be a significant parameter in the efficient ionization of synthetic polymers in ESI. The addition of some salts to the ESI solvent system (e.g., sodium acetate) increases the total ion count in ESI; however, salt concentrations that are too high have been shown to impair the ESI process.[56] Spectra were recorded in positive ion mode with an instrumental resolution of 0.1 amu. All reported molecular weights were calculated via the program package CS ChemDraw 6.0 and are monoisotopic. Simulated isotopic pattern generation was conducted using the Xcalibur program included with the thermoelectron ESI-MS software. The theoretical molecular weight over charge ratios (m/z, assuming $z = +1$) are calculated using the exact molecular mass of the predominant isotope within the structure.

It is important to note that with MMA oligomers the cation (Na^+), which is ubiquitous or provided as a salt in the solvent, binds to the oxygen atoms. More stable configurations are postulated to involve more than one oxygen atom in contact with a cation;[48] thus, the stereochemistry of the polymer may disrupt the ability of the molecule to achieve the configuration needed for high charge states. The number of charges that a given oligomer can accommodate might be affected by the stereochemistry. Such a phenomenon has been shown to hold true for proteins where multicharging has been related to accessibility to basic sites for protonation.[57] However, photopolymerizations at low temperatures yield low-energy stereospecific polymeric species.[58] In free radical polymerization, α,α-disubstituted olefinic monomers usually give rise to syndiotactic polymers owing to the repulsion between the α-methyl group at the polymer end and that of the approaching monomer. Thus, polyMMA primarily consists of syndiotactic triad or *rr* structure, with this syndiotacticity increasing with decreasing temperature.[59]

NMR Spectroscopy. ^{1}H NMR spectra were recorded on a Bruker ACF300 300 MHz spectrometer with $CDCl_3$ used as solvent.

UV−vis Spectroscopy. UV−vis spectra were recorded using a CARY 300 spectrophotometer at 190−500 nm. The solvent was MMA, and the concentration of photoinitiator was close to 5×10^{-3} L mol^{-1} in all cases. Isothermal conditions were maintained at 25 °C using a CARY temperature controller.

Simulations. All simulations have been carried out using the program package PREDICI, version 5.36.4a, on an Intel Pentium M, 1.6 GHz IBM-compatible computer.

Results and Discussion

Prior to the photopolymerizations, the absorption spectra of the initiating system must be considered. If components other than the PI in the formulation (i.e., MMA) absorb light of the same wavelength necessary for the PI excitation, they will compete for the incident light and decrease the efficiency of the initiation process. The absorbance spectra of the PIs used in this study, in bulk MMA, are given in Figure S1 (see Supporting Information) with all the PIs employed absorbing at the incident laser wavelength of 351 nm. The absorption spectrum of MMA was recorded in the region 190−500 nm in acetonitrile solvent at concentrations up to 4.9 M. No monomer absorbance was observed above $\lambda = 300$ nm.

Mass Spectrometric Results. *DMPA-Initiated PLP of MMA.* It is well-known that the initiating radicals in the photolysis of DMPA are generated by a very fast photochemical cleavage reaction followed by secondary fragmentation.[1] The dimethoxybenzyl (acetal) radical can undergo a secondary cleavage to give a methyl radical and methyl benzoate—a reaction that depends on the intensity of the excitation source.[1] Thermal fragmentation of the acetal radical is a slow process at room temperature that becomes dominant with decreasing intensities.[1] Thus, to selectively avoid the formation of byproducts from the photolysis of DMPA and to ascertain the role that the DMPA photolysis products play in initiating and terminating radical chains, low temperatures in conjunction with low irradiation laser intensities are used.

Photopolymerization studies of DMPA initiated MMA by Phan[60,61] have indicated that close to 15% of the dimethoxybenzyl radicals formed from DMPA photolysis are incorporated into the polymer; however, whether they act as initiating or terminating species was not ascertained. Furthermore, these studies show that at least 30% of the benzoyl radicals formed are involved in the polymerization. The methyl radical produced from a secondary fragmentation of the acetal radical has also been seen to contribute to initiation but to a lesser extent than that of the benzoyl fragment.[62,63] Studies by Sander et al.[34] have found methyl benzoate as a major product in photocleavage experiments of DMPA in various solvents. Other major products found included benzil, benzaldehyde, and acetophenone. A study by Baxter et al.[64] using HPLC and GC-MS demonstrated that benzoic acid, methyl benzoate, methyl anisoate, methyl 4-benzoylbenzoate, and methyl 2-benzoylbenzoate are produced. In addition, minute amounts of benzaldehyde, benzophenone, benzyl, acetophenone, and biphenyl were also produced.

As noted, PLP experimental conditions were selected to minimize all possible side reactions associated with photopolymerization, including both chain transfer to monomer and polymer. Using the equation for the chain transfer to monomer constant (C_m) for MMA given by Stickler et al.[13] and extrapolating to −25 °C, one obtains a C_m value of 7.5×10^{-7}. Thus, for approximately 1 in every 75 million propagation steps, a single transfer to monomer step occurs. Under the experimental conditions in the present study (where the largest observed chain lengths are $n = 20$ and conversion is maintained below 3%) chain transfer to monomer is unlikely to be significant. The chain transfer to polymer constant (C_p) for MMA in the temperature range $313 < K < 353$ has been determined to be $(1.5-2.5) \times 10^{-4}$.[14] Thus, for every 15 000 propagation steps at 313 K there is one chain transfer to polymer step. Having used temperatures no higher than 273 K, chain transfer to polymer is also unlikely to be significant in the present study.

The photopolymerization of MMA in the presence of DMPA was conducted at various laser intensities (4−25 mJ/ pulse),[65] frequencies (20 and 100 Hz), initiator concentrations (5.0×10^{-3} and 1.0×10^{-2} mol L^{-1}), and reaction temperatures (0 to −26 °C). Subsequently, ESI-MS was employed to determine the end groups of the polymer chains. The resulting spectra, i.e., product distributions from each experiment, depend on the laser frequency employed and on the irradiation laser intensity. Altering the photoinitiator concentration or reaction temperature did not affect the resulting product distribution significantly.

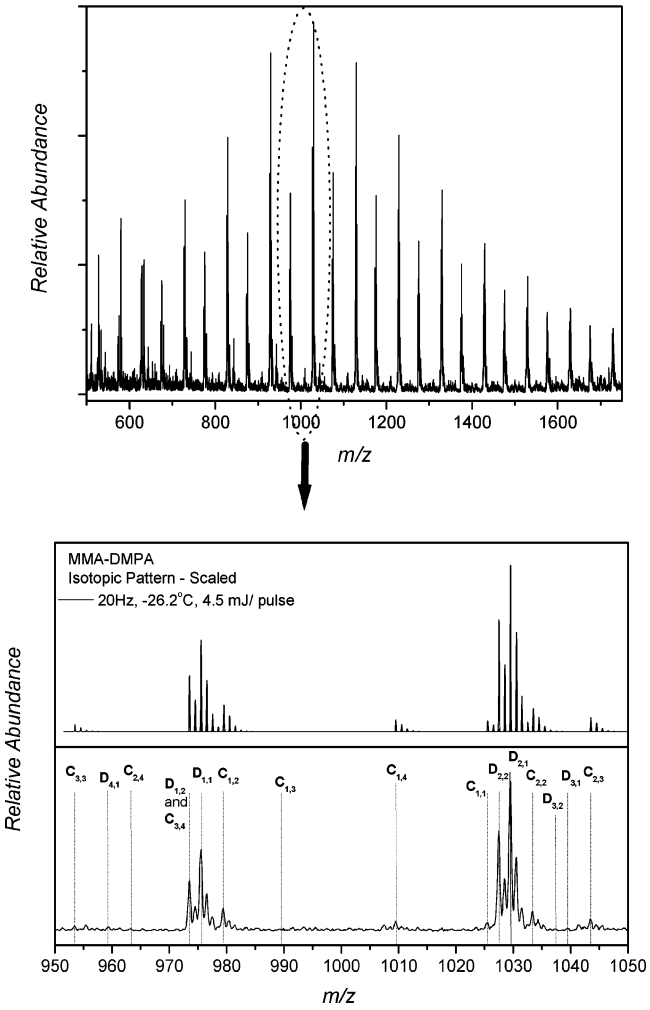
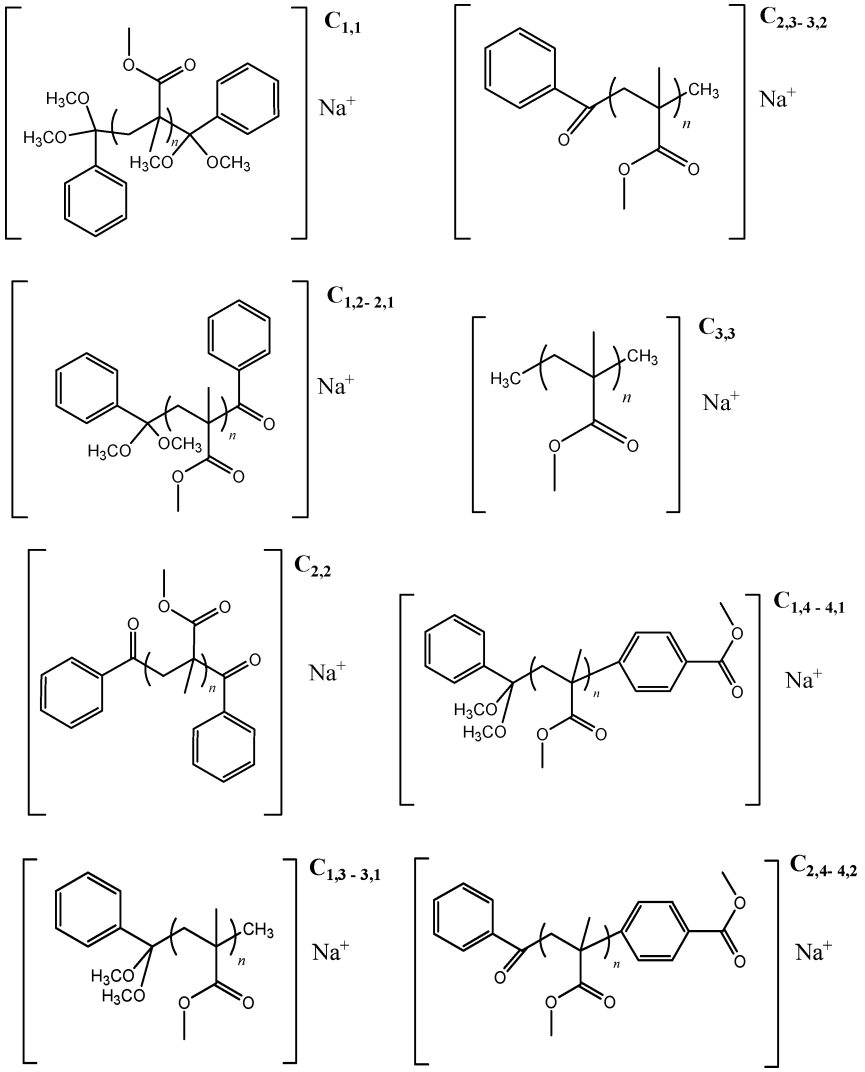


Figure 1. ESI-MS spectrum (lower part) of the polymeric material obtained from the DMPA-initiated ($c_{DMPA,0} = 5 \times 10^{-3}$ mol L^{-1}) PLP of MMA at a laser energy of 4.5 mJ/pulse, a frequency of 20 Hz, and a temperature of −26.2 °C. Simulated isotopic product patterns scaled to experimental result (upper part) are also given. Theoretical product mass-to-charge ratios (*m*/*z*) are indicated by the dotted lines (see Schemes 4 and 5 for the associated structures).

Figure 1 highlights one complete repeat mass unit of polyMMA synthesized by PLP in the presence of DMPA. The spectrum is of exceptionally high resolution (with accuracy of ±0.1 Da), giving clear isotopic patterns for each species present. The photopolymerization was conducted at a temperature of −26.2 °C, a laser intensity of 4.5 mJ/pulse, and a frequency of 20 Hz. Conversion was maintained at <3%. For methacrylates it is known that disproportionation is the dominant biomolecular termination reaction.[32] Possible combination and disproportionation products from the DMPA-initiated photopolymerization of MMA are given in Schemes 4 and 5, respectively.

The nomenclature in the present study is complex. To aid readability, all products which are the same, regardless of the PI from which they have been produced, are labeled identically. For example, all disproportionation products involving the

Scheme 4. Overview of the Possible Combination Product Ions Generated by ESI of the Polymeric Material from the DMPA-Initiated PLP of MMA



benzoyl radical are labeled $D_{2,n}$ regardless of the source of the benzoyl radical. In the case of combination products involving two different end groups, the nomenclature employed gives reference to both groups as there is no way to determine which radical initiated or terminated the polymer chain without further examination of the disproportionation products. That is, $C_{1,2}$, which is akin to $C_{2,1}$, represents a product that terminated via combination and has two different end groups. This product is given as $C_{1,2-2,1}$.

Willemse et al.[32] used peak areas of the mass spectrum to compare the value of the modes of termination in MALDI-ToF-MS analysis of benzoin-initiated PLP-induced copolymerization of MMA and styrene. The use of peak areas in the mass spectrum is justified when looking at a single repeat unit mass within the spectra; however, because of the overlap of the isotopic patters of various different combination and disproportionation products, caution is taken in employing such a technique to give quantitative values of proportions of product formed. Furthermore, signal response discrimination can occur during any of the processes of ionization, transfer of ions to the mass analyzer, mass analysis, and/or ion detection. Thus, there may be some signal response differences associated with end groups, stereochemistry, and branching.[48] Therefore, great care is taken when discussing the relative abundance of particular species determined using the ESI-MS technique, and consequently, such quantities are discussed on a relative basis. The theoretical molecular masses of the combination and disproportionation products for the DMPA-initiated MMA photopolymerizations are given in Table 1.

Figure 1 shows that disproportionation is the favored termination mechanism for the DMPA-initiated PLP of MMA under the reaction conditions investigated. Importantly, Figure 1 also illustrates the presence of quantitative amounts of disproportionation products $D_{1,1}$ and $D_{1,2}$ corresponding to polymer initiated by the acetal fragment of the photolysis of DMPA. Quantitatively, the ratio of disproportionation products $D_{2,1}$:$D_{1,1}$ (and similarly $D_{2,2}$ and $D_{1,2}$) is approximately (based on peak height) 2:1, which implies that the ratio of benzoyl radicals to acetal radicals in initiating the polymerization is 2:1 (assuming that both the acetal- and benzoyl-initiated propagating radicals have equal affinity to terminate via disproportionation). Additionally, the quantity of combination products initiated and terminated by benzoyl radicals ($C_{2,2}$) is approximately equal to that of combination products initiated by a benzoyl radical (or conversely an acetal radical) and terminated by the opposite radical species (i.e., species $C_{1,2-2,1}$). Combination product ($C_{1,1}$) where the polymer is initiated and terminated by an acetal radical is observed in very low amounts. Assuming that all propagating species have an equal affinity to terminate via combination, the quantity of product $C_{2,2}$ being larger than that of $C_{1,1}$ again

Scheme 5. Overview of the Possible Disproportionation Product Ions Generated by ESI of the Polymeric Material from DMPA-Initiated PLP of MMA

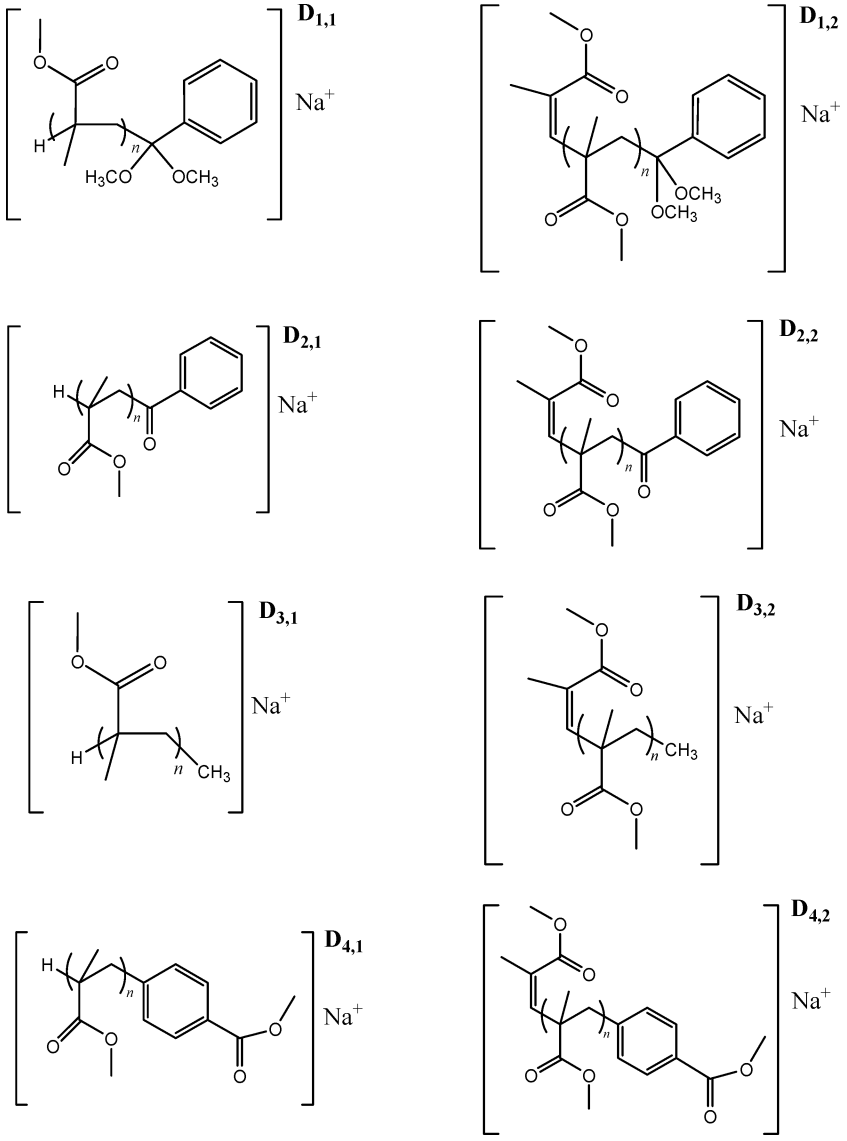


Table 1. Experimental and Theoretical *m*/*z* Values for the Ions Detected by ESI in the DMPA-Initiated PLP of MMA

species	m/z_{theor}	$m/z_{exp(low\ intensity)}$	$m/z_{exp(high\ intensity/freq)}$
$C_{1,1}$	1025.5	1025.5	1025.5
$C_{1,2-2,1}$	979.5	979.4	979.4
$C_{2,2}$	1033.5	1033.4	1033.4
$C_{1,3-3,1}$	989.5		
$C_{2,3-3,2}$	1043.5	1043.5	1043.5
$C_{3,3}$	953.5	953.5	953.5
$C_{1,4-4,1}$	1009.5	1009.5	1009.5
$C_{2,4-4,2}$	963.4		
$C_{3,4-4,3}$	973.5	973.5	973.5
$D_{1,1}$	975.5	975.5	975.5
$D_{1,2}$	973.5	973.5	973.5
$D_{2,1}$	1029.5	1029.5	1029.5
$D_{2,2}$	1027.5	1027.5	1027.5
$D_{3,1}$	1039.6		
$D_{3,2}$	1037.5		
$D_{4,1}$	959.5		959.4
$D_{4,2}$	957.5		

suggests that the benzoyl fragment has a greater affinity to initiate the polymerization than the acetal fragment. Further examination of Figure 1 indicates the presence of quantitative amounts of combination products $C_{2,3-3,2}$, indicating that the acetal fragment has undergone further fragmentation. Interestingly, no ion peaks corresponding to combination products $C_{3,1-1,3}$ ($m/z_{theor} = 989.5$) are found. In considering the low quantitative abundance of the $C_{1,1}$ species, such a finding is not unexpected. Since the acetal fragment undergoes secondary photolysis, it inherently has less opportunity to act as either a terminating or an initiating species.

Unexpectedly, a product with a mass-to-charge ratio, $m/z = 1009.5$, that is congruent with combination product $C_{1,4-4,1}$, i.e., an acetal initiated polymeric species that is terminated by a methyl benzoate fragment (or potentially vice versa), is observed quantitatively in Figure 1. As previously noted, methyl benzoate has been found to be a major product in photocleavage experiments of DMPA in various solvents.[34,64] Therefore, it is possible to envisage a situation where the abundance and nature of byproducts (specifically, methyl benzoate) influences the photopolymerization experiment and radical termination, especially when considering that methyl benzoate has an electrophilic carbonyl group and the phenyl group has the ability to delocalize electrons. Furthermore, the presence of methyl 4-benzoylbenzoate as a decomposition product from DMPA photolysis,[34,64] which may arise from the combination of methyl benzoate (radical) species and a benzoyl radical, indicates that termination processes that feature a reaction of a free radical with methyl

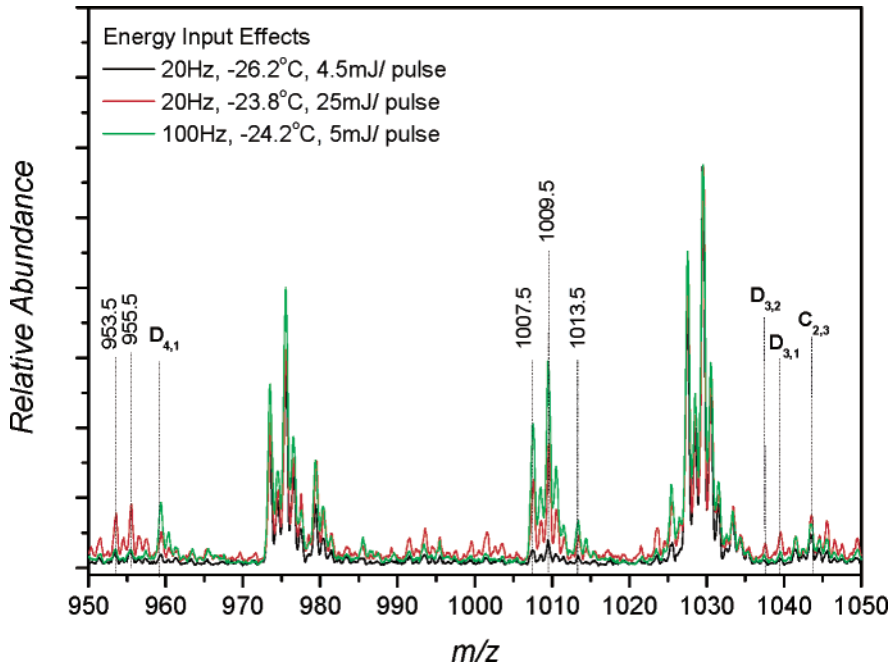


Figure 2. Effect of laser intensity and laser repetition rate on the polymeric material obtained from the DMPA-initiated ($c_{DMPA,0} = 5 \times 10^{-3}$ mol L^{-1}) PLP of MMA. Reaction conditions are given within the figure and the spectra are normalized at $m/z = 1029.5$.

benzoate in the para position on the benzyl ring (and subsequent hydrogen abstraction or similar) may in fact occur. However, if $C_{1,4-4,1}$ is formed, in theory, a corresponding abundance of combination product $C_{2,4-4,2}$ should also be formed. While there exists the possibility of product $C_{1,4-4,1}$ formation, the absence of product $C_{2,4-4,2}$ casts some doubt on this notion, and the peak corresponding to $m/z = 1009.5$ may be attributed to some other termination product. In this context, it is important to note that absence of proof is not necessarily proof of absence. The absence of certain products could be due to their specific end group chemistries that hinder an effective ionization under the conditions employed.

The generation of a complete product spectrum can also be used to investigate the impact, if any, of residual oxygen on the polymer product. Studies on bulk polymerization experiments of DMPA-initiated MMA in the presence of oxygen have shown that benzoylperoxy radicals are formed from benzoyl radicals by oxygen quenching and are involved in the initiation step.[1] Examination of the ESI-MS spectra in Figure 1 shows no evidence of termination products that incorporate either termination or initiation fragments of this nature. The absence of oxygen quenched radical products indicates that oxygen contamination is not a factor influencing product formation in these experiments.

Subsequently, the impact of initiator concentration on radical reactivities was also investigated to determine whether initiator concentration affects the resulting product distribution by influencing the occurrence of side reactions. Initiator concentration was doubled from 5×10^{-3} to 1×10^{-2} mol L^{-1} under the conditions used in Figure 1. No comparative change in the resulting product spectrum was observed.

An interesting observation to note for the DMPA experiment in Figure 1 was that upon UV light exposure after PLP the sample turned yellow. The yellowing of coatings cured with benzil ketals (such as DMPA) has been found to increase upon exposure to UV light and has been attributed to secondary reactions of residual photoinitiator not completely consumed in the photocuring process.[1]

Effect of Energy Input on DMPA-Initiated PLP of MMA. A change in energy input into the photopolymerization system may have a pronounced effect on the reactivity of the photolysis products of DMPA and side reactions involving these species. Energy input into the reaction system can be altered by manipulating the intensity and/or frequency of the incident radiation. Consequently, reaction conditions used to obtain the spectra in Figure 1 were maintained and, independently, the frequency of incident light and radiation laser intensity were increased 5-fold from 20 to 100 Hz and 5 to 25 mJ/pulse, respectively. The resulting product spectra, as well as the spectra shown in Figure 1, are depicted in Figure 2. The conditions used were chosen specifically such that the overall increase in energy input into the system (compared to that of the experiment shown in Figure 1 (100 mW)) were identical in both cases (i.e., 500 mW corresponding to a 5-fold increase).

Figure 2 indicates that the product spectrum of the resulting synthetic polymer becomes significantly more complex with increasing frequency or increasing intensity, congruent with a previous MALDI-ToF-MS analysis of polyMMA synthesized via PLP using DMPA.[38] Incident light frequency is found to influence the amount and type of reactions in MMA photopolymerizations initiated with DMPA. What is markedly evident from examination of Figure 2 is that product peaks at $m/z =$ 959.4, 1007.5, 1009.5, and 1013.5 appear/increase with higher energy input into the system. Disproportionation product $D_{4,1}$ is congruent with and may be attributed to the peak obtained at $m/z = 959.4$. Unexpectedly, what are certainly disproportionation products at $m/z = 1007.5$ and 1009.5 are observed in significant amounts. As discussed previously, the peak at $m/z = 1009.5$ may be attributed to combination product $C_{1,4-4,1}$; however, when the peak at $m/z = 1007.5$ appears at higher energy inputs, this possibility seems unlikely as peaks that differ by exactly 2 amu are characteristic of disproportionation products with the same end grouping. At this point the product corresponding to the peak at $m/z = 1013.5$ is indeterminate.

In an attempt to identify disproportionation terminated polyMMA products with a suitable end grouping such that the

m/*z* value of the polymer chains corresponds to 1007.5 and 1009.5, several disproportionation peaks were investigated from the possible rearrangement and decomposition of DMPA and MMA. Double and higher charge states were also examined, yielding no *m*/*z* value congruent with *m*/*z* = 1007.5 and 1009.5 (see Experimental Section). Also, cationization by alternate cations was considered. In a previous study of polyesters using ESI, it was observed that when THF is used, cationization by K^+ is sometimes enhanced, leading to more complex ESI spectra.[56] Calculation of the theoretical *m*/*z* ratios for K^+ and H^+ cationization products does not assign any of the experimental peaks observed in the spectra shown in Figure 2. In examining further the spectra in Figure 2, an increase in incident laser energy results in a change in product formation similar to that observed for increasing laser frequency. Such an observation is interesting, and it is postulated that these peaks result as a consequence of further fragmentation of the photoinitiator and/or monomer with higher energy input into the system. The increased frequency experiments having a similar effect to that of the increased intensity experiments on polymeric product produced may imply that a photomultiplying effect is taking place.

Effect of Temperature on DMPA-Initiated PLP of MMA. To obtain the desired molecular weights via PLP for ESI-MS analysis, it is necessary to use a frequency applicable across a wide temperature range. A frequency of 100 Hz was chosen and a temperature range of 24 °C examined. Examination of Figure 3 shows that the types of products produced are independent of temperature under the irradiation conditions studied. However, keeping in mind that ESI-MS is a semiquantitative tool, the quantity of disproportionation products incorporating the acetal fragment ($D_{1,1}$ and $D_{1,2}$) and the quantity of the unassigned peaks at *m*/*z* = 1007.5, 1009.5, and 1013.5 increases when going from −24.2 to 0 °C. The disproportionation peaks at *m*/*z* = 1007.5 and 1009.5 are examined further throughout this article. Subsequent experiments give depth to the investigation of the photopolymerization products obtained from the DMPA-initiated PLP of MMA via a judicial choice of PIs, while simultaneously providing a more thorough investigation of radical reactivities.

Benzil-Initiated PLP of MMA. Benzil was used to initiate MMA photopolymerization as it was anticipated that photocleavage would yield, in the absence of hydrogen donors, only benzoyl radicals.[66,67] The resulting product spectra for three photoinitiated polymerizations of MMA using benzil as PI under conditions similar to those employed for the DMPA-initiated PLP of MMA in Figure 2 are presented in Figure 4.

Once again, Figure 4 shows that disproportionation is the dominant termination mechanism in the PLP of MMA. Furthermore, increased laser intensity and laser frequency also result in the appearance of product peaks at *m*/*z* = 1007.5, 1009.5, and 1013.4. These peaks were not quantitatively present at lower laser intensities and frequencies. However, their relative amount is less than that observed for the DMPA/MMA system under similar conditions, suggesting that these peaks may arise partially from interactions with the benzoyl group and/or monomer undergoing some form of fragmentation. Furthermore, there is a quantitatively substantial amount of termination by combination with significant amounts of product $C_{2,2}$ observed, denoting that termination by combination is more prevalent in the benzil than the DMPA-initiated MMA system under the same conditions. Additionally, Figure 4 shows that small quantities of an unexpected combination product $C_{2,3-3,2}$ are observed at all conditions studied, begging the question as to the source of the methyl radials. Theoretical and experimental *m*/*z* values of the combination and disproportionation product ions of the benzil-initiated PLP of MMA are given in Table S2 (see Supporting Information).

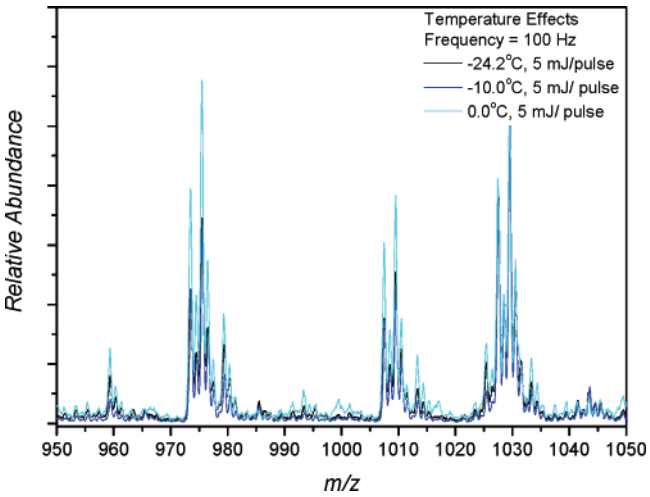


Figure 3. Effect of temperature on the polymeric material obtained from DMPA-initiated ($c_{DMPA,0} = 5 \times 10^{-3}$ mol L^{-1}) PLP of bulk MMA. Laser energies of close to 5 mJ/ pulse and a frequency of 100 Hz were used in all instances. Temperatures are given within the figure. The results are normalized at *m*/*z* = 1029.5.

Benzoin-Initiated PLP of MMA. The photopolymerization of MMA in the presence of benzoin was conducted at conditions similar to that of the DMPA- and benzil-initiated MMA systems. The mass spectra obtained are shown in Figures 5 and 6. Possible termination products resulting from the ether radical are depicted in Scheme 6. Theoretical and experimental *m*/*z* values of the combination and disproportionation product ions of the benzoin-initiated MMA photopolymerization are given in Table S3 (see Supporting Information).

The polymer mass spectrum in Figure 5 suggests that the benzoin-initiated MMA photopolymerization undergoes termination almost exclusively via disproportionation under the conditions investigated, supporting claims by Willemse et al.[31] The almost complete absence of the combination products $C_{5,2-2,5}$ at *m*/*z* = 1035.5 implies that the ether fragment (see Scheme 3B) is not involved significantly in termination events. Willemse et al.[32] found in a MALDI-ToF-MS study of benzoin-initiated PLP of MMA and styrene that the polymer chains resulting from termination by combination consist primarily of two benzoyl radicals with chains consisting of both a benzoyl and an ether end group also found. It must be noted that the experiments by Willemse et al. were conducted at different experimental conditions than those presented here; i.e., higher temperatures (15.2 °C), higher laser energies (40−60 mJ/ pulse), lower laser frequencies (4−12 Hz), and a comonomer system (MMA−styrene) were used. The radical reactivity of the benzoin fragments toward styrene most likely will be different.

There is an isotopic overlap between the mass peaks associated with the disproportionation products capped with the benzoyl and ether radicals produced by the photodecomposition of benzoin (that is, products $D_{5,2}$ and $D_{2,1}$) obscuring the ability to ascertain which is the true product. However, the presence of disproportionation product $D_{2,2}$ incorporating the benzoyl fragment implies that product $D_{2,1}$ must also be present. Furthermore, considering that the quantity of $D_{2,2}$ is significantly greater than that of $D_{2,1}$ (where the quantities of $D_{2,1}$ and $D_{2,2}$ should theoretically be equal) product $D_{5,2}$ and consequently $D_{5,1}$ must also be present, indicating that the ether fragment also initiates the polymerization.

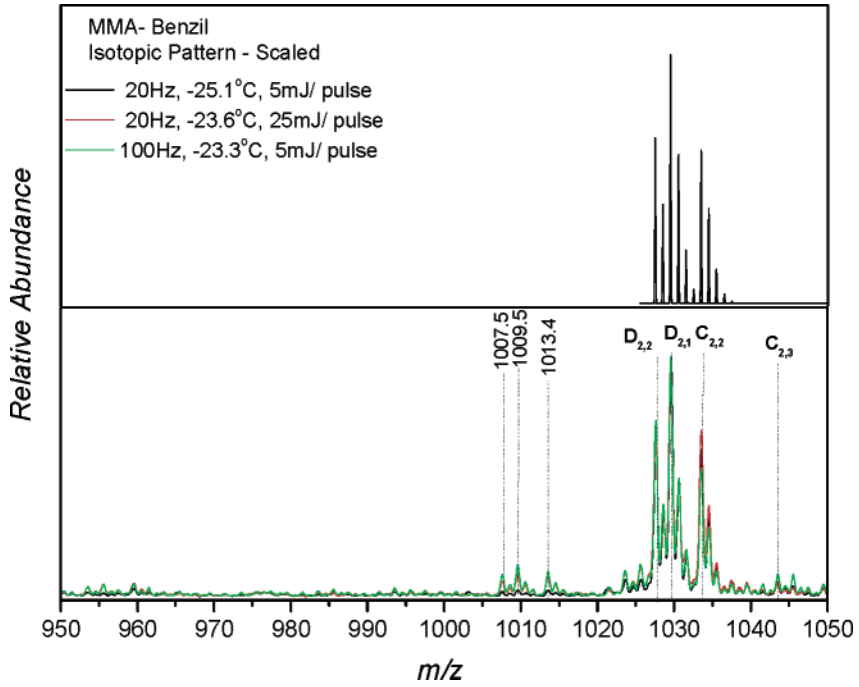


Figure 4. Effect of incident laser intensity and frequency of irradiation on the polymeric material obtained from the benzil-initiated ($c_{benzil,0} = 5 \times 10^{-3}$ mol L^{-1}) PLP of bulk MMA (lower part). Reaction conditions are given within the figure. The isotopic pattern for the theoretical products are given in the upper part of the figure and have been scaled to the experimental results obtained from the reaction at −25.1 °C, 20 Hz, and 5 mJ/pulse. The results are normalized at $m/z = 1029.6$, and theoretical product-to-charge ratios are indicated by the dotted lines.

Scheme 6. Overview of the Possible Termination Product Ions Generated via ESI of the Polymeric Material from the Ether Type Radical in the Benzoin-Initiated PLP of MMA

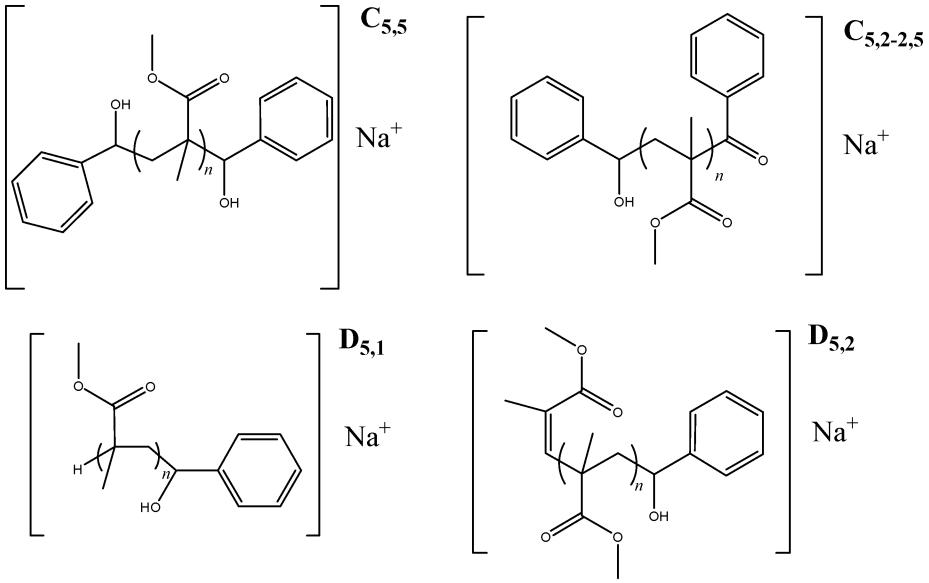


Figure 6 shows that increasing energy input into the system for the benzoin-initiated PLP of MMA, as is the case when DMPA and benzil are used as PIs, again yields a more complex product spectrum. Similarly, the disproportionation products at $m/z = 1007.5$ and 1009.5 are observed in quantitative amounts when either higher laser frequencies and/or laser pulse energies are employed.

BEE-Initiated PLP of MMA. BEE was used to determine whether a change in the structure of the ether type fragment significantly affects the PI reactivity (compared to that of DMPA and benzoin) under the conditions used to probe the photolysis product radical reactivity of the other PI/MMA systems. As in the case of DMPA photolysis, it is important to consider that the behavior of the radical species produced upon photocleavage of BEE may be temperature dependent. Thus, the experiments were carried out under analogous conditions to that of the other PI/MMA systems. Theoretical and experimental m/z values of the combination and disproportionation product ions of the BEE-initiated PLP of MMA are given in Table S4 (see Supporting Information), and the termination products for the BEE-initiated PLP of MMA incorporating the ether radical are given in Scheme 7.

Figure 7 displays that termination predominantly occurs via disproportionation. Importantly, the presence of quantitative amounts of disproportionation products ($D_{6,1}$ and $D_{6,2}$) corresponding to polymer initiated by the ether fragment of the photolysis of BEE are observed. Furthermore, there are more disproportionation products involving the benzoyl fragment ($D_{2,1}$

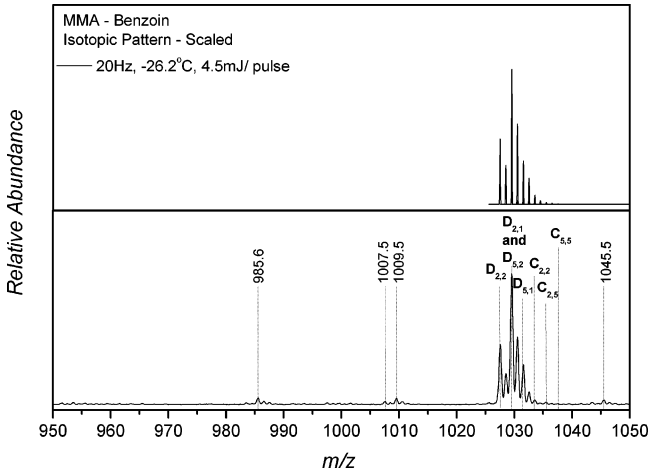


Figure 5. ESI-MS spectrum of the polymeric material obtained from the benzoin-initiated ($c_{benzoin,0} = 5 \times 10^{-3}$ mol L^{-1}) PLP of bulk MMA at −26.2 °C with a laser energy of 4.5 mJ/pulse and a frequency of 20 Hz (lower part). The simulated isotopic product pattern, scaled to experimental result, is given in the upper part of the figure. Theoretical product mass-to-charge ratios (m/z) are indicated by the dotted lines (see Schemes 4−6 for the associated structures).

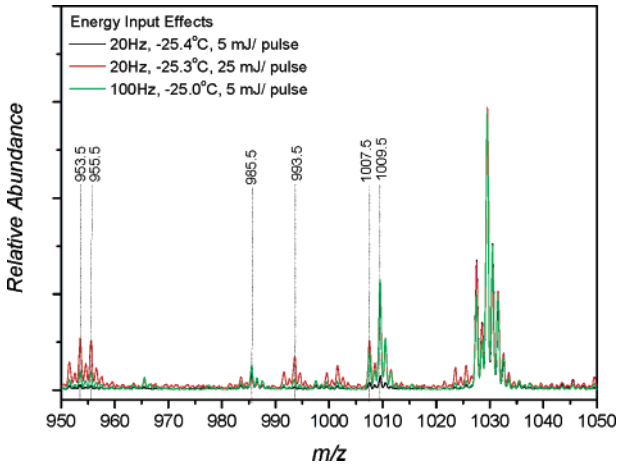
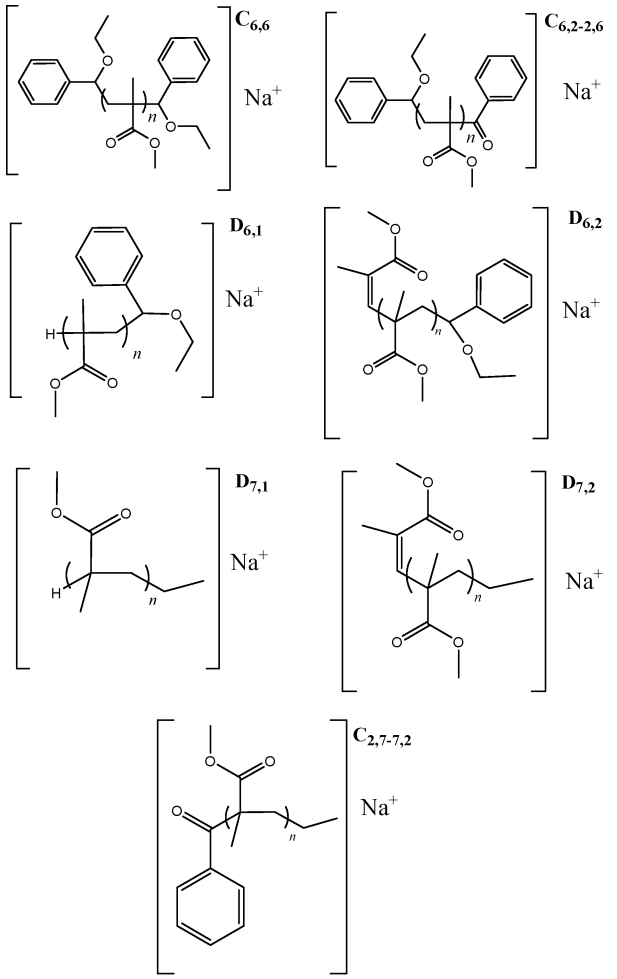


Figure 6. Effect of incident laser intensity and frequency of irradiation on the polymeric product obtained from the benzoin-initiated ($c_{benzoin,0} = 5 \times 10^{-3}$ mol L^{-1}) PLP of bulk MMA. Reaction conditions are given within the figure. The results are normalized at $m/z = 1029.5$.

and $D_{2,2}$) than the ether fragment ($D_{6,1}$ and $D_{6,2}$), suggesting that the benzoyl fragment is the more reactive radical species. Quantitative amounts of combination products dominated by combination product $C_{2,2}$ with very small amounts of combination product $C_{6,6}$ are also observed.

Examination of Figure 8 demonstrates, once again, that increasing either the frequency of irradiation or laser intensity results in a more complex product spectrum. As well, a slight increased proportion of termination by combination—specifically, combination products $C_{6,6}$ and $C_{6,2}$—was observed. Further, the appearance of a quantitative amount of a product peak at $m/z = 1053.6$, congruent with disproportionation product $D_{7,1}$, may indicate that the ether type radical produced from BEE photolysis may have undergone further fragmentation to produce an ethyl radical which has initiated polymerization. However, this is unlikely considering the absence of a product peak $D_{7,2}$ at $m/z = 1051.6$ and in considering that such a radical would tend to act as a predominantly terminating moiety, albeit no combination products involving this species are found. The peaks at $m/z = 1055.5$ and 1053.6 (i.e., $D_{7,1}$) are congruent with products F and E, respectively, in Scheme 9. The origin of such initiating species is discussed later in the text. The peak at m/z

Scheme 7. Overview of the Possible Termination Product Ions Generated via ESI of the Polymeric Material from the Ether Type Radical in the BEE-Initiated PLP of MMA



$= 1043.5$ is congruent with a benzoyl-initiated methyl-terminated chain (or potentially vice versa, i.e., $C_{2,3-3,2}$). The origin of the methyl radical species is unclear. Possibly an ethyl radical produced from the fragmentation of the ether radical species fragments further to give a methyl radical or the monomer itself fragments to yield a CH_3 radical.

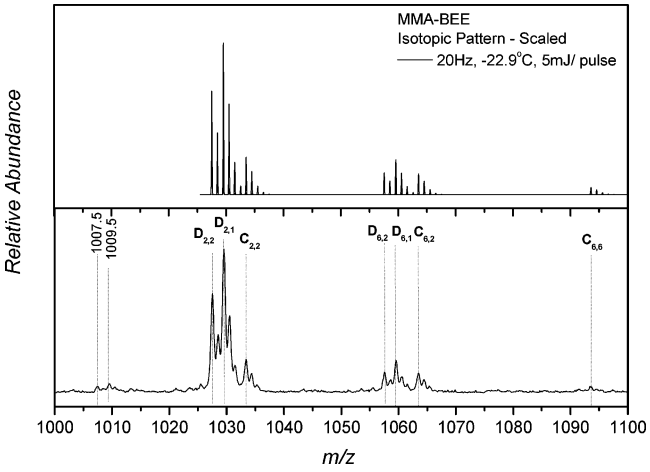


Figure 7. ESI-MS spectrum of the polymeric material obtained from the benzoin ethyl ether-initiated ($c_{BEE,0} = 5 \times 10^{-3}$ mol L^{-1}) PLP of bulk MMA at −22.9 °C, a laser energy of 5 mJ/ pulse, and a frequency of 20 Hz (lower part). The simulated isotopic product pattern, scaled to experimental result, is given in the upper part of the figure. Theoretical product mass-to-charge ratios are indicated by the dotted lines (see Schemes 4, 5, and 7 for the associated structures).

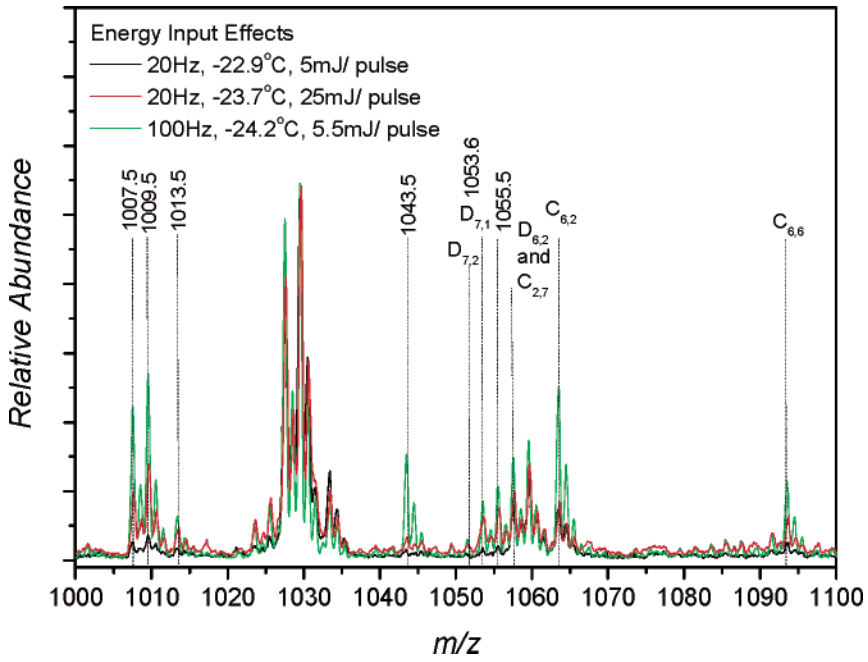
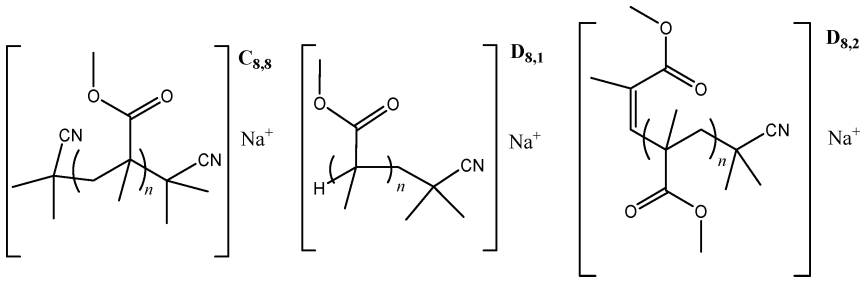


Figure 8. Effect of incident laser intensity and frequency of irradiation on the polymeric product obtained from the benzoin ethyl ether-initiated ($c_{BEE,0} = 5 \times 10^{-3}$ mol L^{-1}) PLP of bulk MMA. Reaction conditions are given within the figure. The results are normalized at $m/z = 1029.5$. Theoretical product mass-to-charge ratios are indicated by the dotted lines.

Scheme 8. Overview of the Possible Termination Product Ions Generated by ESI of the Polymeric Material from the AIBN-Initiated PLP of MMA



As was found in the DMPA-, benzil-, and benzoin-initiated MMA polymerizations, disproportionation peaks at $m/z = 1007.5$ and 1009.5 as well as a peak at $m/z = 1013.5$ are observed at higher laser frequencies and intensities for the BEE-initiated MMA system. Increasing the temperature of the reaction from −23.4 to −10 °C while maintaining a frequency of 100 Hz and a laser energy of 5 mJ/ pulse does not influence significantly the type of products produced (see Figure S2 of the Supporting Information).

DMPA-Initiated PLP of n-Butyl Methacrylate (n-BMA). To determine whether the disproportionation products at $m/z = 1007.5$ and 1009.5 involve monomer specific end groups, experiments were conducted employing *n*-butyl methacrylate (*n*-BMA) under similar conditions to those used for the PI/MMA systems. The observation of similar disproportionation products in the DMPA-initiated PLP of *n*-BMA may indicate an end group generated by an initiation sequence involving the monomer. The resulting ESI-MS data are shown in Figure 9.

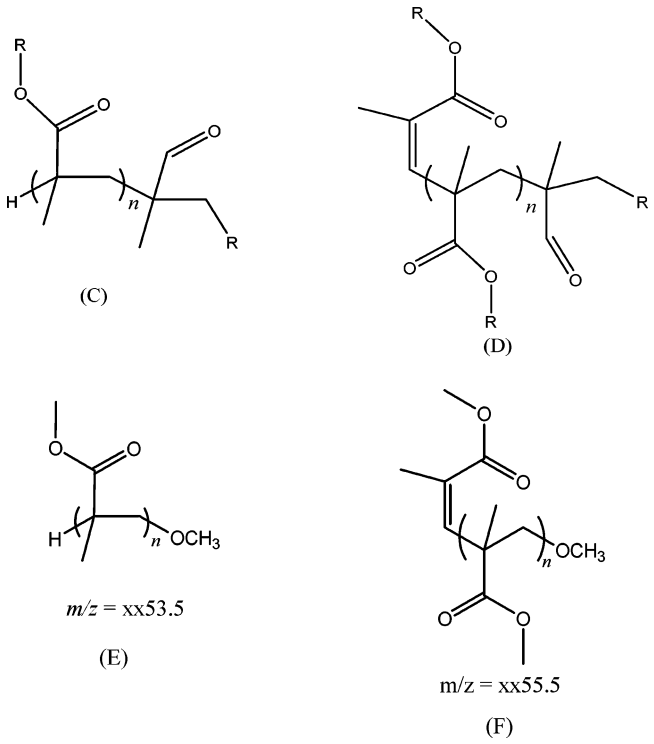
The ESI-MS spectra in Figure 9 indicate that, as in the case of the DMPA-initiated MMA systems, the benzoyl radical is more reactive than the acetal radical. Again, disproportionation products incorporating both the acetal and benzyl fragments are observed, indicating that the acetal and benzoyl fragments both initiate the polymerization. All product peaks in Figure 9 are assigned analogous to Schemes 4 and 5 where MMA is replaced with *n*-BMA, with the exception of what appear to be disproportionation peaks at $m/z = 1285.9$ and 1288.0. These peaks are congruent with structures C and D in Scheme 9 and are discussed later. Theoretical and experimental m/z values for the combination and disproportionation product ions of the DMPA-initiated *n*-BMA photopolymerization are given in Table S5 (see Supporting Information). The product distributions obtained from the DMPA-initiated PLP of *n*-BMA are, as for the DMPA/MMA system, found to increase in complexity with increasing laser irradiation energy and/or repetition rate.

AIBN-Initiated PLP of MMA. To determine whether the previously observed trend of increased product spectrum complexity with increasing laser intensity and/or frequency is related to the non-benzoyl fragment in the PIs examined, MMA was photopolymerized using an azo-initiator (AIBN). Conditions akin to those used to examine the other photoinitated MMA systems were adopted. The resulting mass spectra are depicted in Figure 10.

As with all the PIs examined, the spectra presented in Figure 10 have exceptionally high resolution. The polymeric structures corresponding to termination products for the AIBN-initiated PLP of MMA are given in Scheme 8. Theoretical and experimental m/z values of the combination and disproportionation product ions of the AIBN-initiated PLP of MMA are given in Table S6 (see Supporting Information).

Examination of Figure 10 again indicates that termination predominantly occurs via disproportionation for the AIBN-

Scheme 9. Possible Disproportionation Products (C and D) Congruent with the Peaks of PolyMMA and Poly-*n*-BMA (m/z_{MMA} = 1007.5, 1009.5 and m/z_{n-BMA} = 1285.9, 1288.0, Where R = CH_3 for MMA and C_4H_9 for *n*-BMA) from DMPA-Initiated PLP (C and D) and Methoxy-Initiated Polymer Chains Terminated by Disproportionation in the PLP of MMA (E and F)



initiated PLP of MMA. Notably, in this system, laser intensity and/or laser frequency are found *not to* affect the resulting polymeric material; however, an increase in the proportion of termination by combination (i.e., an increase in termination product $C_{8,8}$) is observed. Furthermore, at higher laser intensities and frequencies there is a near absence of product peaks at *m*/*z* = 1007.5 and 1009.5.

Discussion of Product Peaks. Analysis of the polymeric product profiles has demonstrated that the occurrence of side reactions in DMPA-, benzoin-, BEE-, and benzil-photoinitiated MMA polymerization systems increase with increasing laser intensity and/or laser frequency. In examining Figures 2 and 9 (DMPA-initiated MMA and *n*-BMA systems) the presence of combination product $C_{2,3}$ involving the methyl radical is observed, but disproportionation products ($D_{3,1}$, $D_{3,2}$) involving $^{\bullet}CH_3$ are not seen in any conclusive quantities. Thus, we conclude tentatively that the generated methyl radical acts as a predominantly terminating species—a finding that is congruent with early studies that predict an excess of terminating species in DMPA-initiated polymerizations.[33,37] Moreover, increasing laser intensity and/or frequency is found to result in lower monomer conversion, supporting the hypothesis of the production of a terminating species. In light of such observations, the fate of the methyl radical may indeed be more complex. One can envisage a situation where the methyl radical initiates the polymerization and due to its reactivity and higher energy input into the system (resulting from increased laser frequency and/or laser intensity) results in the cleavage of the methoxy group of the MMA unit closest to the methyl radical. Such a species would result in an aldehyde (or possibly alcohol) species at one end of the polymer chain (see Scheme 9C,D). This possibility is considered due to the fact that disproportionation species with such a structure are congruent with that of the observed peaks at *m*/*z* = 1007.5 and 1009.5 (see Scheme 9C,D) as well as providing an alibi for the generated CH_3. However, ^{1}H NMR studies conducted on the polymeric species produced under the high-energy input conditions in Figure 2 gave no evidence for the presence of an aldehyde or alcohol. Despite this, the postulated theory as to the assignment of the peaks at *m*/*z* = 1007.5 and 1009.5 is strengthened when examining mass spectra obtained from the DMPA-initiated PLP of bulk *n*-BMA. At both high laser intensities and frequencies, the appearance of large quantitative amounts of what are again disproportionation products at m/z_{n-BMA} = 1285.9 and 1288.0 are observed. These structures are perfectly congruent with (as in the case of MMA)

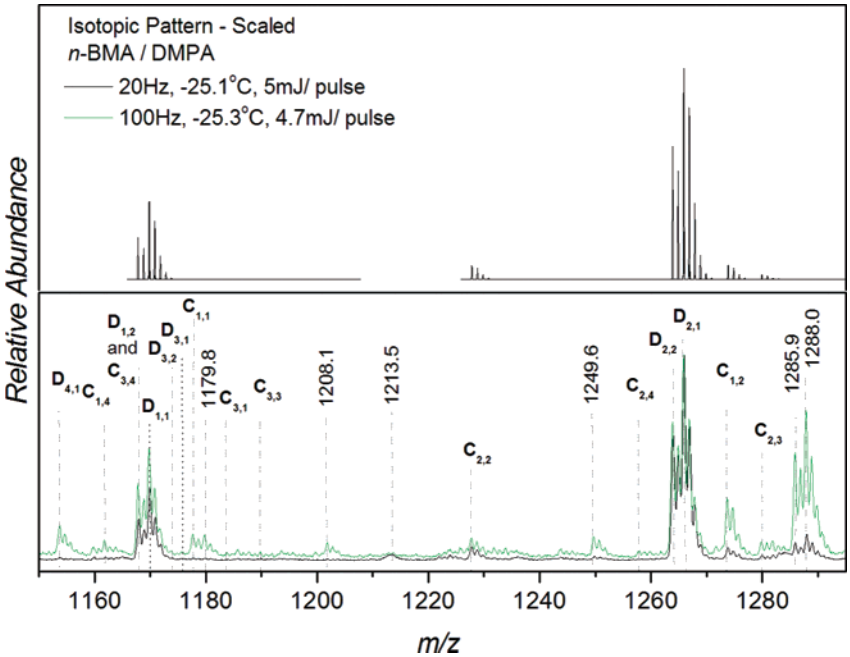


Figure 9. ESI-MS spectra of polymeric material obtained from DMPA-initiated ($c_{DMPA,0} = 5 \times 10^{-3}$ mol L^{-1}) PLP of bulk *n*-BMA (lower part). The reaction conditions are given within the figure. The theoretical isotopic pattern distribution, scaled to the experimental result (−25.1 °C, 20 Hz, 5 mJ/pulse), is given in the upper part of the figure. The results are normalized at *m*/*z* = 1265.9, and theoretical product mass-to-charge ratios are indicated by the dotted lines.

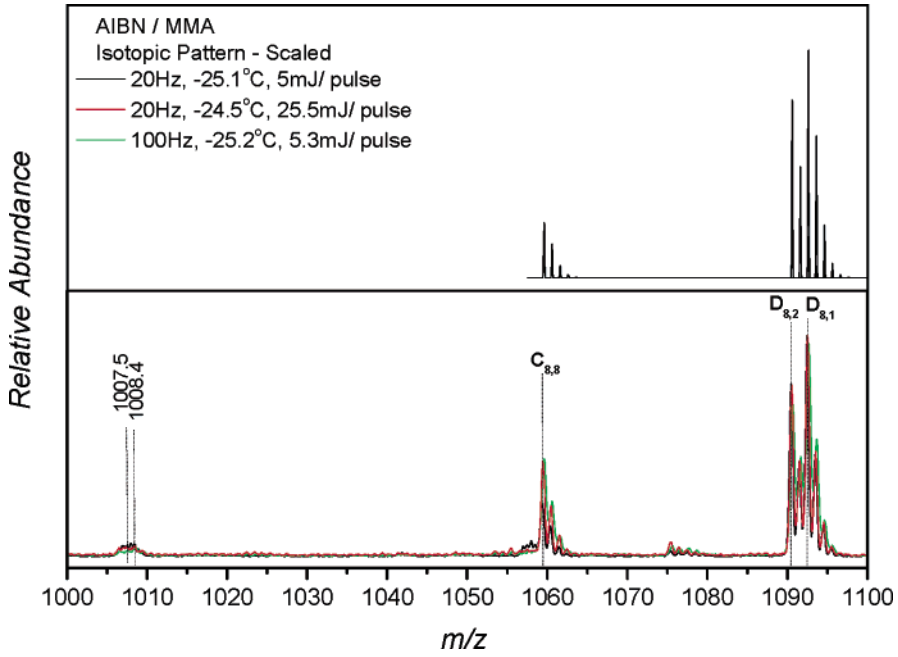


Figure 10. ESI-MS spectrum of polymeric material obtained from the AIBN-initiated ($c_{AIBN,0} = 5 \times 10^{-3}$ mol L^{-1}) PLP of bulk MMA (lower part). The reaction conditions are given within the figure. The theoretical isotopic pattern distribution scaled to the experimental result (−25 °C, 20 Hz, 5 mJ/ pulse) is given in the upper part of the figure. The results are normalized at $m/z = 1092.6$, and theoretical product mass-to-charge ratios are indicated by the dotted lines.

products C and D in Scheme 9, where R (a methyl species for MMA) is replaced with a butyl chain. In considering such possibilities, in the case of MMA, the cleaved methoxy radical may itself be involved in the initiation or termination process. For instance, it may abstract a hydrogen to form methanol, terminate, or initiate a reaction. In examining Figure 2 where DMPA is the PI used, the observed peaks at $m/z = 953.5$ and 955.5 (in the high-intensity experiment) are congruent with the disproportionation products E and F in Scheme 9. Incidentally, structures E and F also appear in the high-energy input experiments in the benzoin- and BEE-initiated MMA systems (see Figures 6 and 8, respectively). Structures E and F given in Scheme 9 for the benzoin-initiated PLP of MMA are only possible if a methoxy radical is somehow produced in the photoinitiation process. The only foreseen route of this occurring (in the benzoin−MMA system at least) is from fragmentation of the MMA monomer itself, suggesting that monomer fragmentation may occur at high-energy inputs.

Inferred from the present studies of the peaks at $m/z_{MMA} = 1007.5$ and 1009.5 for the PI/MMA systems is the following: (i) The species at $m/z_{MMA} = 1007.5$, 1009.5 and $m/z_{n-BMA} = 1285.9$, 1288.0 are disproportionation peaks of products having the same end grouping, attributable to the fact that that for both MMA and *n*-BMA the peaks are exactly 2 amu apart. The molecular formula of these end groups is C_5H_9O and $C_8H_{15}O$ for MMA and *n*-BMA, respectively. These formula were found to be the only chemically realistic formulation of end group structure using C, O, and H to obtain such molecular weights. (ii) If the products are associated with the benzoyl fragment they should occur in the same quantitative proportions for DMPA as in the photoinitiated polymerization of MMA with benzil, which undergoes photolysis to give benzoyl fragments only. Conversely, if the products were associated with the non-benzoyl fragment, these peaks would *not* occur in the photoinitiated polymerization of MMA with benzil. In the benzil-initiated PLP of MMA, the quantitative presence of peaks at $m/z_{MMA} = 1007.5$ and 1009.5 was found to be less under the same conditions as that for the DMPA-initiated MMA system. Therefore, their quantitative appearance must—in the majority—be attributable to the non-benzoyl photolysis products of the various PIs. With all PIs except the azo photoinitiator AIBN, quantitative amounts of disproportionation products at $m/z = 1007.5$ and 1009.5 are produced under high-energy inputs, thus implying the formation of these products on the alkyl methacrylate monomer in the presence of a PI which undergoes photolysis to give a benzoyl fragment. (iii) The generated products are *not* the result of fragmentation of the polymeric species under the conditions employed in the ESI. If fragmentation did occur during ESI, a substantially more complex product spectrum would result, irrespective of the sample preparation mode prior to MS analysis. **(**iv**)** MS-MS analysis of the polymeric product peak at $m/z = 1009.5$ provides fragments corresponding to methanol and the loss of complete monomer units.

Conclusions

Vital and novel information in regard to the radical reactivities of the photolysis products produced from various common photoinitiators toward methyl methacrylate at low temperatures, synthesized using PLP and examined using ESI-MS, are presented. The effects of UV laser intensity, laser repetition rate, and temperature on radical reactivity of the photolysis products produced have been investigated. Both the benzoyl and acetal fragments generated as a result of the photocleavage of DMPA were found to act as initiating and probable terminating species. Under the conditions studied, the acetal radical produced in DMPA photolysis is fragmented further to yield methyl radicals which may act predominantly as terminating moieties. Both the benzoyl and ether fragments produced as a result of the photocleavage of benzoin were found to act as initiating and probable terminating species, indicating that the ether radical fragment does not act exclusively as a terminating species. An increase in deposited energy into the reaction system results in a more complex polyMMA product spectrum with increased proportions and types of various polymer products. The quantity of side reactions is most significant for benzil ketals and benzil

ethers. The chemical composition, distribution, and modes of termination for several PI/MMA systems are mapped successfully, providing the most in-depth and comprehensive information about termination products and photolysis product radical reactivity in photoinitiated MMA polymerizations to date.

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Supporting Information Available: UV−vis spectra of PIs used in this study in MMA and figure showing effect of temperature on polymeric materials; tables of theoretical and experimental masses of products for benzil-, benzoin-, BEE-, and AIBN-initiated PLP of MMA and DMPA-initiated PLP of *n*-BMA. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Gruber, H. F. *Prog. Polym. Sci.* **1992**, *17*, 953−1044.
(2) Kaur, M.; Srivastava, A. K. *J. Macromol. Sci., Part C: Polym. Rev.* **2002**, *42*, 481−512.
(3) Ge, J.; Trujillo, M.; Stansbury, J. W. *J. Dent. Mater.* **2005**, *21*, 1163−1169.
(4) Anseth, K. S.; Newman, S. M.; Bowman, C. N. *Adv. Polym. Sci.* **1995**, *122*, 177−217.
(5) Fisher, J. P.; Dean, D.; Engel, P. S.; Mikos, A. G. *Annu. Rev. Mater. Res.* **2001**, *31*, 171−181.
(6) Anseth, K. S.; Metters, A. T.; Bryant, S. J.; Martens, P. J.; Elisseeff, J. H.; Bowman, C. N. *J. Controlled Release* **2002**, *78*, 199−209.
(7) Buback, M.; Feldermann, A.; Barner-Kowollik, C.; Lacik, I. *Macromolecules* **2001**, *34*, 5439−5448.
(8) Buback, M.; Egorov, M.; Felderman, A. *Macromolecules* **2004**, *37*, 1768−1776.
(9) Szablan, Z.; Stenzel, M. H.; Davis, T. P.; Barner, L.; Barner-Kowollik, C. *Macromolecules* **2005**, *38*, 5944−5954.
(10) Lissi, E. A.; Garrido, J. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 391−393.
(11) Beuermann, S.; Buback, M.; Davis, T. P.; Gilbert, R. G.; Hutchinson, R. A.; Olaj, O. F.; Russell, G. T.; Schweer, J.; Van Herk, A. M. *Macromol. Chem. Phys.* **1997**, *198*, 1545−1560.
(12) Buback, M.; Kowollik, C. *Macromolecules* **1998**, *31*, 3211−3215.
(13) Stickler, M.; Meyerhoff, G. *Makromol. Chem.* **1978**, *179*, 2729−2745.
(14) Corner, T. *Adv. Polym. Sci.* **1984**, *62*, 95−142.
(15) Caykara, T.; Guven, O. *Polym. Degrad. Stab.* **1999**, *65*, 225−229.
(16) Schultz, A. R. *J. Phys. Chem.* **1961**, *65*, 967−972.
(17) Simha, R. *J. Polym. Sci.* **1952**, *9*, 465−467.
(18) David, C.; Fuld, D.; Geuskens, G.; Charlesby, A. *Eur. Polym. J.* **1969**, *5*, 641−648.
(19) Wochnowski, C.; Shams Eldin, M. A.; Metev, S. *Polym. Degrad. Stab.* **2005**, *89*, 252−264.
(20) Hu, Y.; Chen, C. *Polym. Degrad. Stab.* **2003**, *82*, 81−88.
(21) Odian, G. *Principles of Polymerization*; Wiley-Interscience: New York, 1991.
(22) Fouassier, J. P.; Merlin, A. *J. Photochem.* **1980**, *12*, 17−23.
(23) Luís Faria, J.; Steenken, S. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1153−1159.
(24) Heine, H. G. *Tetrahedron Lett.* **1972**, *47*, 4755−4758.
(25) Yee, L. H.; Coote, M. L.; Davis, T. P.; Chaplin. R. P. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2192−2200.
(26) Szablan, Z.; Ah Toy, A.; Terrenoire, A.; Davis, T. P.; Stenzel, M. H.; Müller, A. H. E.; Barner-Kowollik, C. *J. Polym. Sci., Polym. Chem.* **2006**, *44*, 3692−3710.
(27) Davis, T. P.; Matyjaszewski, K. In *Handbook of Radical Polymerization*; Wiley-Interscience: New York, 2002.
(28) Pappas, S. P.; Asmus, R. A. *J. Polym. Sci., Polym. Chem.* **1982**, *20*, 2643−2653.
(29) Carlblom, L. H.; Pappas, S. P. *J. Polym. Sci.* **1977**, *15*, 1381−1391.
(30) Hageman, H. J.; van der Maeden, F. B. J.; Janssen, P. C. *Makromol. Chem.* **1979**, *180*, 2531−2537.
(31) Willemse, R. X. E. Ph.D. Thesis, Technical University of Eindhoven, 2005.
(32) Willemse, R. X. E.; van Herk, A. M. *J. Am. Chem. Soc.* **2006**, *128*, 4471−4480.
(33) Kowollik, C. Ph.D. Thesis, Göttingen, 1999. ISBN 3-89712-705-9.
(34) Sander, M. R.; Osborn, C. L. *Tetrahedron Lett.* **1974**, *5*, 415−418.
(35) Jaegermann, P. Lendzian, F.; Rist, G.; Mõbius, K. *Chem. Phys. Lett.* **1987**, *140*, 615−619.
(36) Fischer, H.; Baer, R.; Hany, R.; Verhoolen, I.; M. J. Walnier, M. J. *J. Chem. Soc., Perkin Trans. 2* **1990**, 787−798.
(37) Buback, M.; Busch, M.; Kowollik, C. *Macromol. Theory Simul.* **2000**, *9*, 442−452.
(38) Barner-Kowollik, C.; Vana, P.; Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 675−681.
(39) Kaji, M.; Muramatsu, Y.; Unno, A.; Hirai, O. *J. Photopolym. Sci. Technol.* **2005**, *18*, 135−140.
(40) Hanton, S. D. *Chem. Rev.* **2001**, *101*, 527−569.
(41) Montaudo, G. *Trends Polym. Sci.* **1996**, *4*, 81−86.
(42) Scrivens, J. H.; Jackson, A. T. *Int. J. Mass Spectrom.* **2000**, *200*, 261−276.
(43) Barner-Kowollik, C.; Davis, T. P.; Stenzel, M. H. *Polymer* **2004**, *45*, 7791−7805.
(44) Nielen, M. W. F. *Mass Spectrosc. Rev.* **1999**, *18*, 309−344.
(45) Raeder, H. J.; Schrepp, W. *Acta Polym.* **1998**, *49*, 272−293.
(46) Tanaka, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 3861−70.
(47) Saf, R.; Mirtl, C.; Hummel, K. *Acta Polym.* **1997**, *48*, 513−526.
(48) McEwen, C. N.; Simonsick, W. J., Jr.; Larsen, B. S.; Ute, K.; Hatada, K. *J. Am. Soc. Mass Spectrom.* **1995**, *6*, 906−911.
(49) Vana, P.; Albertin, L.; Davis, T. P.; Barner-Kowollik, C. *J. Polym. Sci., Polym. Chem.* **2002**, *40*, 4032−4037.
(50) Felderman, A.; Ah Toy, A.; Davis, T. P.; Stenzel, M. H.; Barner-Kowollik, C. *Polymer* **2005**, *46*, 8448−8457.
(51) Ah Toy, A.; Vana, P.; Davis, T. P.; Barner-Kowollik, C. *Macromolecules* **2004**, *37*, 744−751.
(52) Vana, P.; Davis, T. P.; Barner-Kowollik, C. *Aust. J. Chem.* **2002**, *55*, 315−318.
(53) Deleted in proof.
(54) Coote, M. L.; Zammit, M. D.; Davis, T. P. *Trends Polym. Sci.* **1996**, *4*, 189−196.
(55) Olaj, O. F.; Bitai, I.; Hinkelmann, F. *Makromol. Chem.* **1987**, *188*, 1689−1702.
(56) Guittard, J.; Tessier, M.; Blais, J. C.; Bolbach, G.; Rozes, L.; Maréchal, E.; Tabet, J. C. *J. Mass Spectrom.* **1996**, *31*, 1409−1421.
(57) Chowdhury, S. K.; Katta, V.; Chait, B. T. *J. Am. Chem. Soc.* **1990**, *112*, 9012−9013.
(58) Kaur, M.; Srivastava, A. K. *J. Macromol. Sci., Part C: Polym. Rev.* **2002**, *42*, 4, 481−512.
(59) Hatada, K.; Kitayama, T.; Ute, K. *Prog. Polym. Sci.* **1988**, *13*, 189−276.
(60) Phan, X. T. P. *J. Radiat. Curing* **1986**, *18*, 23−25.
(61) Phan, X. T. P. *J. Radiat. Curing* **1986**, *13*, 11−17.
(62) Borer, A.; Kirchmayer, R.; Rist, G. *Helv. Chim. Acta* **1978**, *61*, 305−24.
(63) Groenenboom, C. J.; Hageman, H. J.; Overreem, T.; Weber, A. J. M. *Makromol. Chem.* **1982**, *183*, 281−292.
(64) Baxter, J. E.; Davidson, R. S.; Hageman, H. J.; Havkoort, G. T. M. *Polymer* **1988**, *29*, 1575−1580.
(65) The intensity of the incident radiation is beset with an error of ±30% over the course of a single reaction (20 min) due to gradual heating of the reaction gas in the laser system and/or degradation of laser gas over time as well as some condensation which may occur on the reaction vials due to the low temperatures used.
(66) Hutchinson, J.; Ledwith, A. *Polymer* **1973**, *14*, 405−408.
(67) Mukai, M.; Yamauchi, S.; Hirota, N. *J. Phys. Chem.* **1989**, *93*, 4411−4413.

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