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MALDI−TOF−MS Analysis of Ruthenium(II)-Mediated Living Radical Polymerizations of Methyl Methacrylate, Methyl Acrylate, and Styrene[1]

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ABSTRACT: Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI−TOF−MS) has been employed for the analysis of poly(methyl methacrylate) (PMMA), poly(methyl acrylate) (PMA), and polystyrene (PSt), which were obtained by ruthenium-mediated living radical polymerization. Proper selection of analysis conditions gave well-resolved spectra of these polymers (one m/z separation). The MS spectra of these polymers showed only one series of peaks separated exactly by the mass of monomers. The observed mass of each peak agreed well with the theoretical one, which possesses one initiator fragment at the α-end and one chlorine group (also from the initiator) at the ω-end. The observed isotopic distributions were in good agreement with the simulated distribution based on the polymer structure. On the other hand, the spectra of PMMA, PMA, and PSt prepared by conventional radical polymerization with AIBN showed two or three series resulting from bimolecular radical termination and uncontrolled initiation.

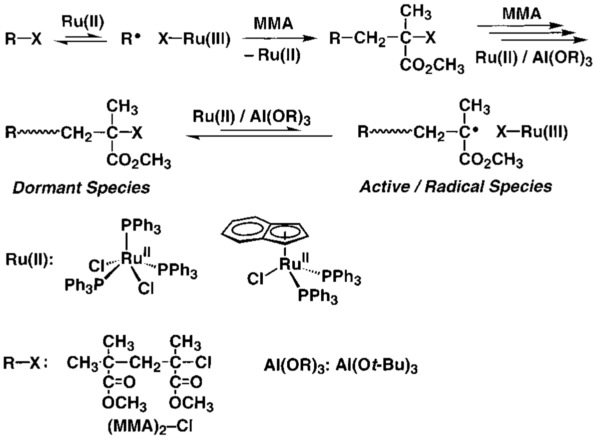
Introduction

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI−TOF−MS) has now been employed for a wide variety of synthetic polymers as well as proteins.[2,3] This can tell us absolute molecular mass, which is difficult to measure by other methods such as size-exclusion chromatography (SEC) and can also provide valuable information about the repeat units and the terminal groups of polymers. This would lead to further clarification of polymerization mechanism and is now one of the most attractive and effective tools for polymer analysis.

Living radical polymerization is now one of the most extensively studied subjects in precision polymerization.[4−13] Most of the living radical polymerizations recently developed are based on the reversible activation of dormant species with stable but potentially active covalent bonds that can be activated by heat, light, and catalysts to give growing radicals. These include nitroxide-mediated,[4−6] transition-metal-catalyzed,[6−12] and RAFT[6,13] polymerizations in which their covalent species possess C−ON, C−halogen, and C−SC(S) bonds, respectively. For example, we first reported living radical polymerization mediated by transition-metal complexes such as RuCl$_2$(PPh$_3$)$_3$, where the carbon−halogen terminal is reversibly and homolytically activated via redox reaction between Ru(II) and Ru(III) (Scheme 1).[14,15] The initiating system basically consists of an organic halide (R−X) as an initiator and a transition metal complex as a catalyst, and in some cases employs a metal alkoxide like Al(OR)$_3$ as an accelerator or additive. Similar living polymerizations have been achieved using other complexes of Cu(I), Fe(II), Ni(II), Rh(I), Re(V), etc.[7−11]

MALDI−TOF−MS has recently been employed for the analysis of the polymers obtained by nitroxide-mediated[16−20] and transition-metal-catalyzed polymerizations.[21−32] Some of these studies revealed that carefully selected conditions for MALDI−TOF−MS analysis gave well-resolved spectra that provide structural and molecular mass information not obtainable by other analytical methods.

Scheme 1



In this study, we analyzed the polymers obtained with ruthenium(II) complexes such as RuCl$_2$(PPh$_3$)$_3$ and Ru(Ind)Cl(PPh)$_2$ (Ind = indenyl; η^5-C$_9$H$_7$) by MALDI−TOF−MS in order to investigate our metal-catalyzed living radical polymerizations.[33,34] Methyl methacrylate (MMA), methyl acrylate (MA), and styrene were thus polymerized with the Ru catalysts in conjunction with the chlorine-capped dimer of MMA [(MMA)$_2$−Cl] as an initiator and Al(O-*t*-Bu)$_3$ as an additive.[35] This study shows that the use of 1,8-dihydroxy-9(10*H*)-anthracenone (dithranol) as a matrix and sodium trifluoroacetate as an ionizing agent gives well-resolved MALDI−TOF−MS spectra of these polymers and that the Ru(II)-mediated living radical polymerization affords only one series of polymers that possess one initiator fragment at the α-end and one chlorine at the ω-end without observable side reactions, as expected from the proposed reaction mechanism.[14,15]

Results and Discussion

1. Poly(methyl Methacrylate). (a) Living Polymers. MALDI−TOF−MS was first applied to examine poly(methyl methacrylate) (PMMA) obtained with the (MMA)$_2$−Cl/Ru(Ind)Cl(PPh$_3$)$_2$ initiating system in tolu-

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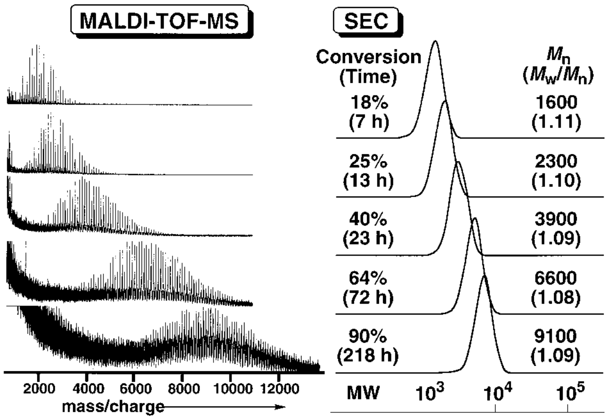
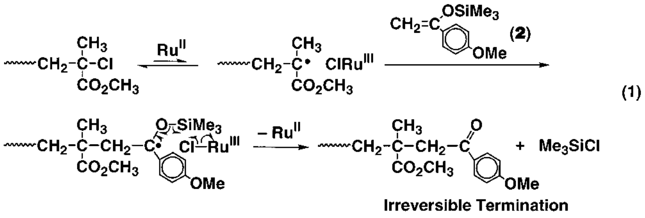


Figure 1. MALDI–TOF–MS spectra and SEC curves of PMMA obtained by living radical polymerization with $(MMA)_2$–Cl/Ru(Ind)Cl$(PPh_3)_2$ (20/4 mM) in toluene at 80 °C. $[MMA]_0$ = 2.0 M.

ene at 80 °C. Under our analysis conditions (see the Experimental), fine spectra with one *m*/*z* resolution were routinely obtained. As observed by size-exclusion chromatography (SEC), the peak maximum of these MS spectra clearly shifted to high molecular weight with increasing monomer conversion (Figure 1). The signal-to-noise ratios decrease for samples obtained at higher conversion, though they have narrow SEC curves. This is due to the difficulty in ionizing high molecular weight polymers.[2,3]

Figure 2a shows the expanded MS spectrum of a PMMA sample obtained at 18% conversion shown in Figure 1. There was one main series of peaks whose interval was regular, ca. 100.1, the molar mass of the monomer. The absolute mass of each peak equals the molecular weight expected for the PMMA with one chlorine atom at the ω-end, one initiator fragment at the α-end, and sodium ion from the salt used for the MS analysis: H–$(MMA)_2(MMA)_n$Cl/Na^+; MMA = $CH_2C(CH_3)(CO_2CH_3)$; cf. structure **1** in Figure 1. Beside the main peak series, two minor series appeared, one of which is supposed to be PMMA that loses the halogen and other group during the MS analysis as shown later. The polymer obtained with another ruthenium catalyst, $RuCl_2(PPh_3)_3$, coupled with $(MMA)_2$–Cl and Al(O-*t*-Bu)$_3$, exhibited a similar spectrum (Figure 2b). This indicates that the two ruthenium complexes generate identical series of polymers.

(b) Quenched Polymers. We have previously reported that the ruthenium-mediated living radical polymerization can be terminated by a silyl enol ether such as **2** which leads to a more stable C–C terminal via elimination of the terminal chlorine (eq 1).[36,37] We then analyzed such a quenched polymer by MALDI–TOF–MS (Figure 2c). The peaks of the chlorine-capped main series completely disappeared, and only one new series appeared, again at 100.1 intervals. The new series is free from the minor peaks observed in Figure 1a with the polymer with a C–Cl terminal. The peak mass of the new series agrees well with the calculated value for structure **3** in Figure 2, i.e., PMMA with ketone at the ω-end and hydrogen or the dimer unit at the α-end. This means that all chlorine terminals in polymer **1** survive without elimination during the polymerization and that they are completely converted to the ketone terminals on quenching with **2**.



(1)

The absence of minor peaks in the spectrum of the ketone-capped polymer **3** (with a more stable terminus) indicates, in turn, that the chlorine-capped polymer **1** is less stable to laser irradiation. MS analysis of one of these minor series further showed that it corresponds to PMMA resulting from chlorine elimination form **1** (eq 2). A similar laser-induced halogen loss has been reported for samples obtained in the copper-catalyzed polymerization[24,25] and other polymers with chlorine.[38] The other minor series (with lower mass) was most probably due to further elimination of methyl group from the terminal methyl ester.

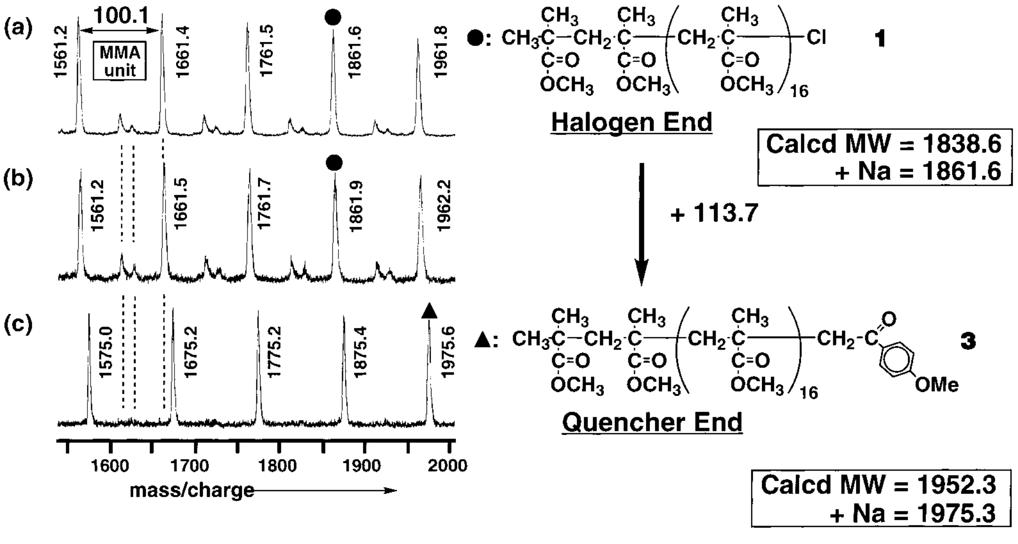


Figure 2. MALDI–TOF–MS spectra at linear mode of PMMA obtained with (a) $(MMA)_2$–Cl/RuCl(Ind)$(PPh_3)_2$ (20/4 mM), M_n = 3900, M_w/M_n = 1.09, (b) $(MMA)_2$–Cl/$RuCl_2(PPh_3)_3$/Al(O-*t*-Bu)$_3$ (40/10/40 mM), M_n = 3400, M_w/M_n = 1.58, and (c) $(MMA)_2$–Cl/$RuCl_2(PPh_3)_3$/Al(O-*t*-Bu)$_3$ (40/10/40 mM) and quencher ($[\text{quencher}]_{\text{add}}$ = 400 mM), M_n = 4000, M_w/M_n = 1.31, in toluene at 80 °C. $[MMA]_0$ = 2.0 M.

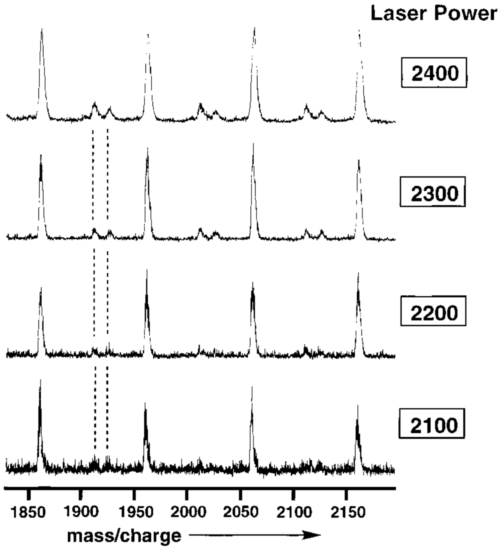


Figure 3. Effects of laser power on the MALDI−TOF−MS spectra at linear mode of PMMA obtained with $(MMA)_2$−Cl/$RuCl_2(PPh_3)_3$/Al(O-*t*-Bu)$_3$ (40/10/40 mM) in toluene at 80 °C. $[MMA]_0 = 2.0$ M, $M_n = 4100$, and $M_w/M_n = 1.44$.

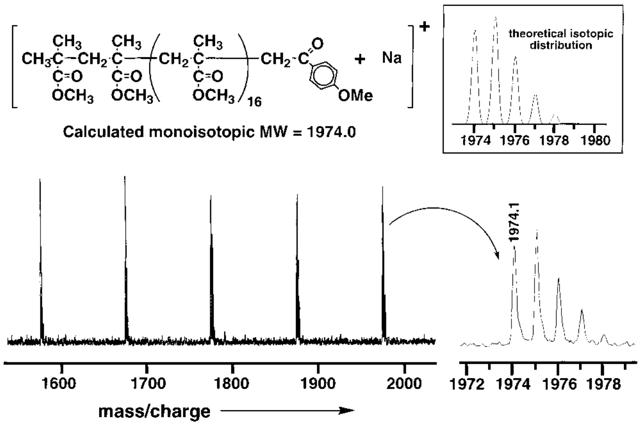


Figure 4. MALDI−TOF−MS spectra at reflector mode of PMMA obtained with $(MMA)_2$−Cl/$RuCl_2(PPh_3)_3$/Al(O-*t*-Bu)$_3$ (40/10/40 mM) $[quencher]_{add} = 400$ mM in toluene at 80 °C. $[MMA]_0 = 2.0$ M, $M_n = 4000$, and $M_w/M_n = 1.31$.

(c) MALDI Analysis Conditions. The effects of the laser intensity on the spectra also suggested the dehalogenation of the chlorine-capped polymer during the MS analysis. The two small series, observed with a laser power of 2400, became negligible at a weaker laser power, 2100 (Figure 3). These results also suggest that the elimination occurs by laser irradiation rather than during the polymerization.

For higher mass resolution, the reflector mode was used for polymer **3** obtained with the quencher (Figure 4). In comparison to Figure 2c, the peak width decreased, and each peak now consisted of a set of peaks with one mass (*m*/*z*) difference, due to the isotope distribution in PMMA molecules of the same degree of polymerization and the terminal structures. The lowest mass of such a peak cluster around $m/z = 1970-1980$ is 1974.1, which is of the monoisotopic 16-mer of PMMA **3** (i.e.; PMMA without D, ^{13}C, and other minor isotopes). The simulated isotopic distribution for the 16-mer (Figure 4, inset) is quite similar to the observed one. These results further demonstrate that the ruthenium-mediated living radical polymerization affords only one series of polymers whose structure is expressed as **1**.

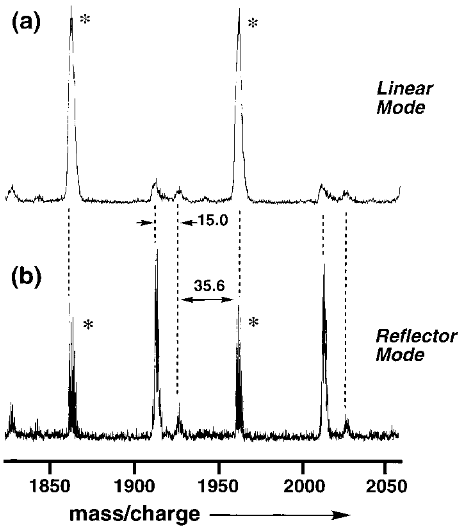


Figure 5. Comparison between the MALDI−TOF−MS spectra at linear (a) and reflector (b) of PMMA obtained with $(MMA)_2$−Cl/$RuCl_2(PPh_3)_3$/Al(O-*t*-Bu)$_3$ (40/10/40 mM) in toluene at 80 °C. $[MMA]_0 = 2.0$ M, $M_n = 3400$, and $M_w/M_n = 1.58$.

The reflector mode was also employed for the PMMA obtained without the quencher (Figure 5). The spectrum (Figure 5b) clearly differs from that of the linear mode (Figure 5a), where the intensity of the chlorine-capped terminal (the asterisked peaks) is weaker in the reflector mode. This is due to the less stable ion of the chlorine-capped polymer partially decomposing during the flight. This again supports dehalogenation during the MS analysis.[38]

(d) Living vs Conventional Radical Polymerizations. Figure 6 compares PMMA samples prepared by conventional and living radical polymerizations. The conventional free radical polymerization was initiated with azobis(isobutyronitrile) (AIBN) in toluene at 80 °C, whereas the living polymerization used the $(MMA)_2$−Cl/$RuCl_2(PPh_3)_3$/Al(O-*t*-Bu)$_3$ initiating system under the same reaction conditions (see Experimental Section). The sample from the conventional polymerization (Figure 6a) shows two series of peaks, which correspond to polymers with cyano groups at either (filled circles) or both (filled triangles) ends, as already reported.[39] The former is generated by disproportionation, and the latter by recombination. In contrast, the ruthenium-based system gave the only one series of polymers (**1**), as already discussed. MALDI analysis thus demonstrated the precision reaction control by the Ru catalysis.

2. Polystyrene. MALDI−TOF−MS analysis was also carried out on polystyrene obtained by AIBN-initiated radical polymerization (Figure 7a) or by $RuCl_2(PPh_3)_3$-mediated polymerization (Figure 7b). The latter afforded only one series, as with PMMA, although the MWDs were broader ($M_w/M_n = 2.20$ by SEC) due to slow interconversion between the dormant and active species in comparison to propagation. However, mass values indicated that the polymers do not carry terminal chlorine but an olefin terminal most probably generated by dehalogenation during MS analysis. We have already confirmed the chlorine-capped structure by ^{1}H NMR.[40] Therefore, the Cl terminal of polystyrene is unstable under MS analysis.

The MS spectrum of polystyrene by conventional radical polymerization (Figure 7a) is more complex and consists of three peak series. In free radical polymerization, recombination is predominant, while dispropor-

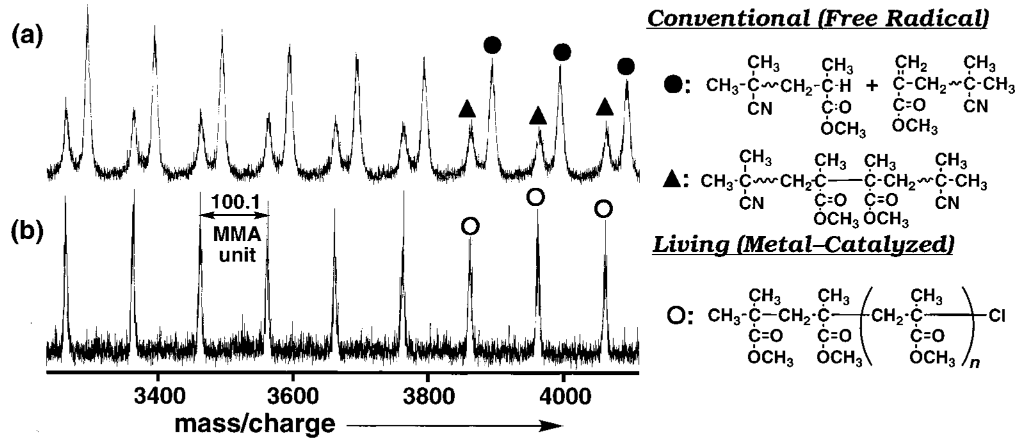


Figure 6. Comparison between the MALDI−TOF−MS spectra between PMMA prepared by AIBN (a) and the ruthenium-based system (b). Key: (a) AIBN (200 mM) in toluene at 80 °C: $[\mathrm{MMA}]_0 = 2.0$ M, $M_n = 2500$, $M_w/M_n = 2.68$; (b) $(\mathrm{MMA})_2{-}\mathrm{Cl}/\mathrm{RuCl}_2(\mathrm{PPh}_3)_3/\mathrm{Al}(\mathrm{O}\text{-}t\text{-}\mathrm{Bu})_3$ (40/10/40 mM) in toluene at 80 °C. $[\mathrm{MMA}]_0 = 2.0$ M, $M_n = 4100$, and $M_w/M_n = 1.44$.

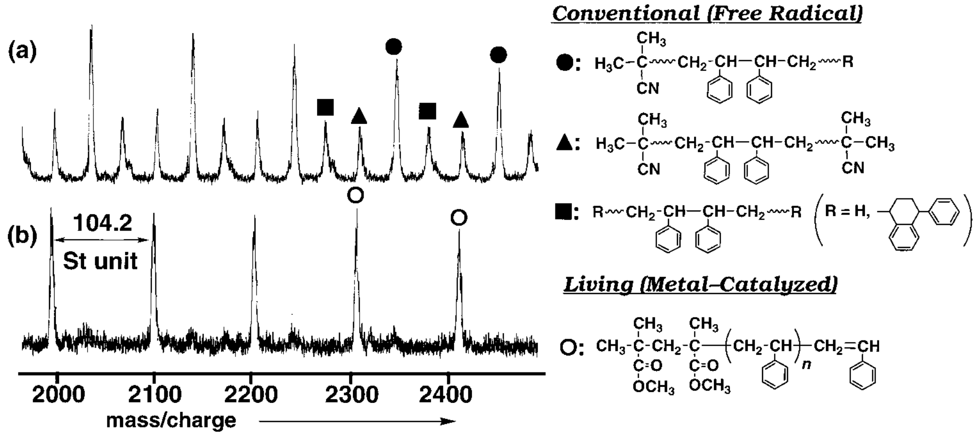


Figure 7. Comparison between the MALDI−TOF−MS spectra between polystyrene prepared by AIBN (a) and the ruthenium-based system (b). Key: (a) AIBN (200 mM) in toluene at 80 °C: $[\mathrm{styrene}]_0 = 2.0$ M, $M_n = 1700$, $M_w/M_n = 1.63$; (b) $(\mathrm{MMA})_2{-}\mathrm{Cl}/\mathrm{RuCl}_2(\mathrm{PPh}_3)_3/\mathrm{Al}(\mathrm{O}\text{-}t\text{-}\mathrm{Bu})_3$ (40/10/40 mM) in toluene at 80 °C. $[\mathrm{styrene}]_0 = 2.0$ M, $M_n = 6000$, and $M_w/M_n = 2.20$.

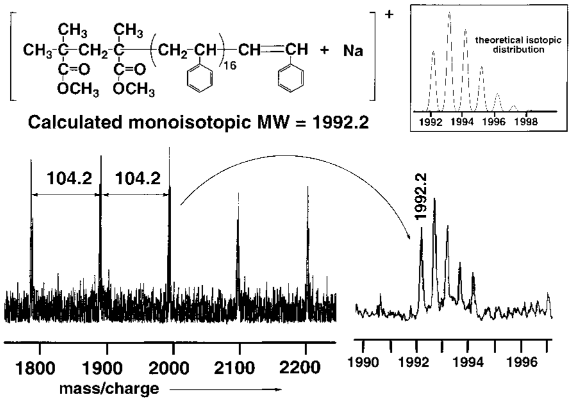


Figure 8. MALDI−TOF−MS spectra in reflector mode of polystyrene obtained with $(\mathrm{MMA})_2{-}\mathrm{Cl}/\mathrm{RuCl}_2(\mathrm{PPh}_3)_3/\mathrm{Al}(\mathrm{O}\text{-}t\text{-}\mathrm{Bu})_3$ (40/10/40 mM) in toluene at 80 °C. $[\mathrm{styrene}]_0 = 2.0$ M, $M_n = 6000$, and $M_w/M_n = 2.20$.

tionation is negligible, and there are two modes of initiation, the AIBN-induced and the thermal initiation via a Diels−Alder reaction.[39,41] The three possible terminal structures are illustrated in Figure 7a.

Figure 8 shows expanded MS spectra in the reflector mode for a polystyrene sample obtained by the living radical polymerization. Fine one-mass resolution is attained for each main-peak cluster, and for example, a cluster of well-resolved peaks can be seen around $m/z = 1900{-}2000$, which is attributed to a set of isotopic homologues of polystyrene with 16 styrene repeat units (16-mers). In this cluster, the peak of the smallest mass appears at $m/z = 1992.2$, nearly the same as that of the monoisotopic 16-mer with the α-end $\mathrm{H{-}(MMA)_2}$- unit, the ω-end olefin, and a sodium cation. The olefinic ω-end observed in the MALDI analysis indicates that the benzylic halogen terminus of polystyrene is less stable upon laser ionization than the PMMA counterpart. As already shown by ^{1}H NMR,[40] the unsaturated ω-end does not come from side-reactions during the polymerization, and this point may be further confirmed by quenching, such as with **2** for the PMMA living/dormant ends.

3. Poly(methyl Acrylate). Similar analysis was also carried out on PMA obtained with the $(\mathrm{MMA})_2{-}\mathrm{Cl}/\mathrm{RuCl}_2(\mathrm{PPh}_3)_3/\mathrm{Al}(\mathrm{O}\text{-}t\text{-}\mathrm{Bu})_3$ system (Figure 9). The Ru-generated polymer (Figure 9b) led to a single series of PMA chains, in contrast to another sample obtained with AIBN under similar conditions, which consists of two series (Figure 9a) due to disproportionation and recombination (filled circles and triangles).

We also analyzed the PMA obtained with the ruthenium-system in the reflector mode (Figure 10). The observed isotopic distribution was similar to the theoretical distribution for the PMA structure expected for the living polymerization. Namely, the observed peak cluster around $m/z = 2066$ corresponds to the 21-mer of PMA for the structure $\mathrm{H{-}(MMA)_2(MA)_\mathit{n}Cl}$. However,

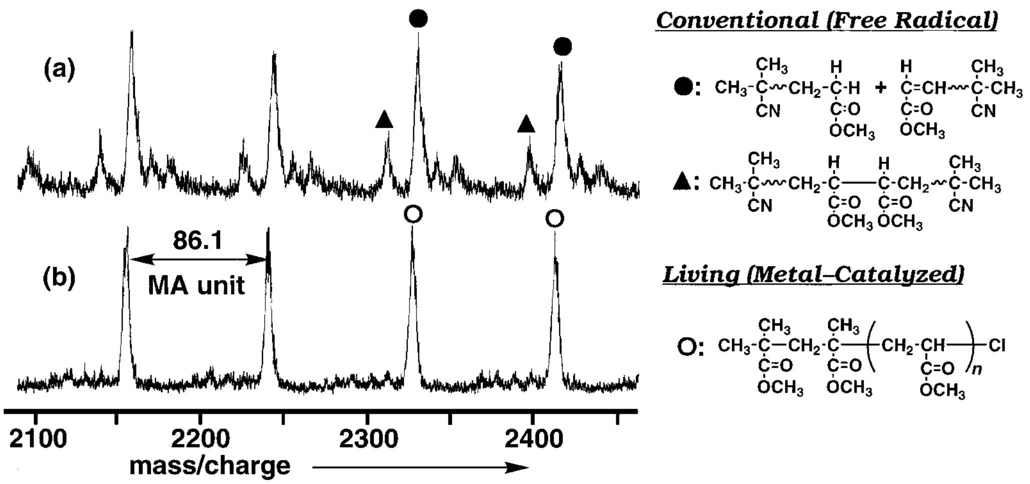


Figure 9. Comparison between the MALDI–TOF–MS spectra between PMA prepared by AIBN (a) and the ruthenium-based system (b). Key: (a) AIBN (200 mM) in toluene at 80 °C: $[\mathrm{MA}]_0 = 2.0$ M, $M_n = 4900$, $M_w/M_n = 6.07$; (b) $(\mathrm{MMA})_2$–Cl/$\mathrm{RuCl_2(PPh_3)_3}$/$\mathrm{Al(O}$-t-$\mathrm{Bu)_3}$ (40/10/40 mM) in toluene at 80 °C. $[\mathrm{MA}]_0 = 2.0$ M, $M_n = 3000$, and $M_w/M_n = 1.75$.

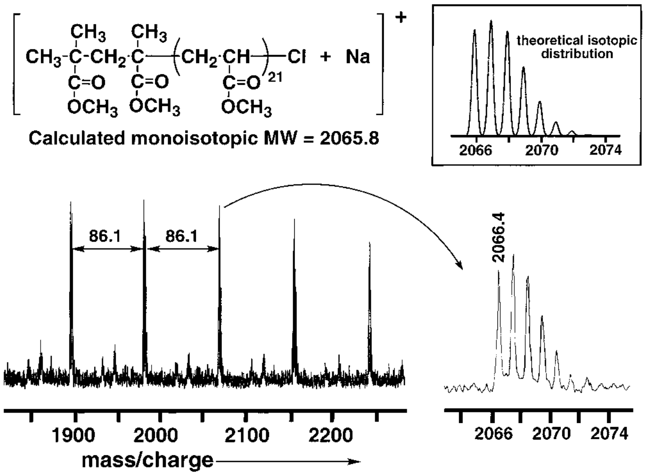


Figure 10. MALDI–TOF–MS spectra in reflector mode of PMA obtained with $(\mathrm{MMA})_2$–Cl/$\mathrm{RuCl_2(PPh_3)_3}$/$\mathrm{Al(O}$-t-$\mathrm{Bu)_3}$ (40/10/40 mM) in toluene at 80 °C. $[\mathrm{MA}]_0 = 2.0$ M, $M_n = 3000$, and $M_w/M_n = 1.75$.

additional minor series are seen, probably due to the partial loss of the chlorine ω-end. The relative amount of the dehalogenated peak is much smaller than those for the PMMA (Figure 5) and the polystyrene (Figure 8) even though the spectrum is measured in the reflector mode. This suggests that C–Cl terminal of PMA is relatively stable during MS analysis.

In conclusion, MALDI–TOF–MS analysis elucidated the polymer structure, especially the terminal structure, in the ruthenium-mediated living radical polymerization as well as in conventional radical polymerization. The analysis is now applicable not only to PMMA, but also polystyrene and PMA. The $\mathrm{RuCl_2(PPh_3)_3}$-based system afforded just one series of polymers, which possess one initiator unit at the α-end and one chlorine ω-end. This also confirms our proposed mechanism for the living radical polymerization via the ruthenium-catalyzed reversible activation of the carbon–halogen terminal.

Experimental Section

MALDI–TOF–MS. MALDI–TOF–MS was performed on a PerSeptive Biosystems Voyager DE-STR equipped with 2-m linear and 3-m reflector flight tubes and a 337-nm nitrogen laser (pulse width, 3 ns), along with a delayed extraction capability. All experiments were carried out at an accelerating potential of 20 kV in both linear and reflector modes. In general, mass spectra from 256 laser shots were accumulated summed to produce a final spectrum. Angiotensin I (human; MW = 1296.5) (BACHEM) and insulin (bovine pancreas 28.3; MW = 5733.50) (Nacalai) were used as internal standards to calibrate the mass scale.

Samples for MALDI–TOF–MS analysis were prepared by mixing the polymer, a matrix, and a cationizing agent in a solvent. For example, a PMMA sample (approximately 10 mg/mL) was dissolved in THF. The matrix [1,8-dihydroxy-9(10*H*)-anthracenone; dithranol] and the cationizing agent (sodium trifluoroacetate) were also dissolved separately in THF (30 and 10 mg/mL, respectively). A 30 μL portion of the PMMA solution, 90 μL of the matrix solution, and 30 μL of the cationizing agent were mixed in a glass vial. The weight ratio of polymer/matrix/cationizing agent was thus 1/9/1. Then 0.5 μL portions of the mixture were deposited onto 10–20 wells of the gold-coated sample plate and dried in air at room temperature. The same procedures were also applied to polystyrene and PMA.

Materials. MMA (Tokyo Kasei; >99%), styrene (Wako; >99%), and MA (Tokyo Kasei; >99%) were dried overnight over calcium chloride (MMA and MA) or anhydrous sodium sulfate (styrene), and distilled twice from calcium hydride under reduced pressure before use. $\mathrm{RuCl_2(PPh_3)_3}$ (Merck; >99%), $\mathrm{Ru(Ind)Cl(PPh_3)_2}$ (Strem; >98%), and $\mathrm{Al(O}$-t-$\mathrm{Bu)_3}$ (Tokyo Kasei; >99%) were used as received and handled in a glovebox under a moisture- and oxygen-free argon atmosphere ($\mathrm{H_2O} < 1$ ppm; $\mathrm{O_2} < 1$ ppm). Dimethyl 2-chloro-2,4,4-trimethylglutarate [$(\mathrm{MMA})_2$–Cl, initiator] was prepared and recrystallized from hexane.[34] Toluene (Wako; >99%) was dried overnight over calcium chloride, distilled over sodium benzophenone. The internal standards for gas chromatography, *n*-octane (Wako; >99%) and tetralin (Wako; >98%), were dried overnight over calcium chloride, distilled twice over calcium hydride, and bubbled with dry nitrogen for more than 15 min immediately before use. The quencher, 1-trimethylsilyloxy-1-*p*-methoxyphenylethene (**2**), was prepared as reported and distilled before use.[36,37] 1,8-Dihydroxy-9(10*H*)-anthracenone (Aldrich; >97%), sodium trifluoroacetate (Tokyo Kasei; >98%), and THF (Wako; free from a stabilizer, >99.5%) were used for MALDI–TOF–MS analysis.

Polymerization Procedures. Polymerization was carried out by the syringe technique under dry nitrogen in baked glass tubes equipped with a three-way stopcock or in baked and sealed glass vials. A typical example for MMA polymerization with the $(\mathrm{MMA})_2$–Cl/$\mathrm{RuCl_2(PPh_3)_3}$/$\mathrm{Al(O}$-t-$\mathrm{Bu)_3}$ is given below. In a 50 mL round-bottomed flask was placed $\mathrm{RuCl_2(PPh_3)_3}$ (71.91 mg, 0.0750 mmol) and toluene (2.31 mL), *n*-octane (0.23 mL), MMA (1.61 mL), and solutions of $(\mathrm{MMA})_2$–Cl (0.35 mL of 859 mM in toluene, 0.30 mmol) and $\mathrm{Al(O}$-t-$\mathrm{Bu)_3}$ (3.00 mL of

100 mM in toluene, 0.30 mmol) were added sequentially in this order at room temperature under dry nitrogen. The total volume of the reaction mixture was thus 7.5 mL. Immediately after mixing, aliquots (1.5 mL each) of the solution were injected into baked glass tubes, which were then sealed (except when a stopcock was used) and placed in an oil bath kept at 80 °C. In predetermined intervals, the polymerization was terminated by cooling the reaction mixtures to −78 °C. In the case of the termination by the quencher, the solution of **2** (0.465 mL of 1.29 M in toluene, 0.60 mmol) was injected into glass tubes through a three-way stopcock by the syringe technique under nitrogen. Glass tubes were shaken vigorously just after addition of quencher, and placed for 12 h in an oil bath kept at +80 °C. Then glass tubes were cooled to −78 °C. Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography with *n*-octane or tetralin as internal standards. The quenched reaction solutions were diluted with toluene (ca. 20 mL) and rigorously shaken with an absorbent [KYOWAAD-2000G-7 ($Mg_{0.7}Al_{0.3}O_{1.15}$); Kyowa Chemical Industry] (ca. 5 g) to remove the metal-containing residues. After the absorbent was separated by filtration (Whatman 113V), the filtrate was washed with water and evaporated to dryness to give the products, which were subsequently dried overnight under vacuum at room temperature. Polymer yield was lower than that expected from conversion because of partial loss of polymer during the workup.

Measurements. The MWD, M_n, and M_w/M_n values of polymers were measured in chloroform at 40 °C on three polystyrene gel columns [Shodex K-805L (pore size: $10-10^5$ Å; 8.0 mm i.d. × 30 cm) × 3; flow rate 1.0 mL/min] connected to a Jasco PU-980 precision pump and a Jasco 930-RI refractive index and 970-UV ultraviolet detectors. The columns were calibrated against 11 standard poly(MMA) samples (Polymer Laboratories; $M_n = 630-220\,000$; $M_w/M_n = 1.06-1.22$) or 11 standard polystyrene samples (Pressure Chemical; $M_n = 580-1\,547\,000$; $M_w/M_n = 1.1$) as well as the monomers. The poly(MMA) calibration was also applied to poly(MA). Polymer samples for MALDI−TOF−MS analysis were fractionated by preparative SEC (column: Shodex K-2002) to be free from catalyst residues without loss of oligomers if present.

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References and Notes

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