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Silyl Enol Ethers: End-Capping Agents for Living Radical Polymerization of Methyl Methacrylate with Ruthenium Complex[1]

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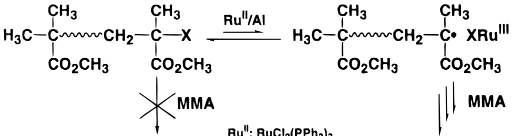
Introduction. Living polymers may be “quenched” with suitable end-capping agents, such as chlorosilanes for living carbanions,[2] malonate anions for living carbocations,[3,4] and nitroxides for free radicals.[5] In most cases the products are end-functionalized polymers where a residue of the quencher is covalently connected to the polymer’s ω-end; multifunctional quenchers will lead to multicomponent block copolymers, star polymers, and polymer networks, among numerous possible polymer architectures. In addition to these synthetic applications, quenching or end-capping in living polymerization, albeit selective and quantitative, is of parallel importance in fundamental study, permitting precise and quantitative determination of the nature, concentration, lifetime, and possible decay of the growing species.

To warrant these synthetic and analytical advantages, quenchers should meet at least the following criteria: the quenching reaction should be quantitative, selective, and specific toward the growing ends without side reactions such as degenerative chain transfer and hydride or proton abstraction; the reaction should be reasonably faster than the concurrent propagation; the terminal residue from the quencher should be connected to the ω-end through stable covalent linkages that are able to withstand the environment of the subsequent workup and polymer recovery procedures; and preferably, the terminal group thus generated can be spectroscopically quantified by NMR, UV/visible, or other methods. This work is to find suitable quenchers (end-capping agents) for metal-mediated living radical polymerizations of methacrylates and related monomers that we have currently been developing.

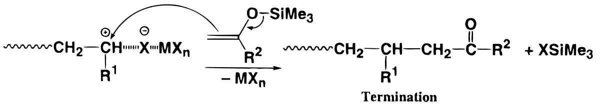
Recently, we have found transition metal-mediated living radical polymerizations of methacrylates,[6−8] styrene,[9] and other monomers (eq 1).[10] The initiating systems for these living processes consist of an alkyl halide (R−X; initiator) and a transition metal complex;[11] sometimes an aluminum compound such as aluminum alkoxide is additionally employed. Typically, the combination of bromotrichloromethane (CCl_3Br), a ruthenium complex [dichlorotris(triphenylphosphine)ruthenium, $RuCl_2(PPh_3)_3$], and aluminum isopropoxide [$Al(O\textit{i}Pr)_3$] induces living polymerization of methyl methacrylate (MMA) to give polymers of controlled molecular weights and narrow molecular weight distributions (MWDs). As schematically illustrated in eq 1, the ruthenium complex interacts with the halogen X in the initiator (R−X) to generate an initiating radical $R^{\bullet}$ from which propagation begins. The growing polymers involve relatively stable carbon−halogen terminal linkages (−C−X; dormant species), originating from the initiator, that are considered to reversibly dissociate into the growing radical ($-C^{\bullet}$; active species) via the assistance of the ruthenium complex and possibly in conjunction with the aluminum compound. These dormant and active species are in equilibrium and rapidly interchanging during propagation.



(1)

According to our recent study, the living MMA polymerization with $RuCl_2(PPh_3)_3$ is terminated with stable radicals such as galvinoxyl or nitroxide radicals, whereas it remains undisturbed in the presence of an excess of methanol or water.[12] Despite the efficient quenching, these stable radicals do not combine to the polymer ends but abstract the β-hydrogen, leaving an exo double bond. It is therefore unknown which types of compounds are suitable as quenchers that fulfill the above-specified criteria in the transition metal-mediated living radical polymerizations.

This study is the first examination of silyl enol ethers as quenchers for living radical polymerization. In our systems, like living cationic polymerization systems invloving halogen terminals,[3,13] the carbon−halogen bonds at propagating ends are reversibly converted into active species. For living cationic polymerization under these conditions, we have already reported those silyl enol ethers [$CH_2{=}CR(OSiMe_3)$; R = Ph, etc.] are good quenchers, which react with carbocations to result in terminal ketones ($-C-CH_2-COR$) by releasing trimethylsilyl halide (eq 2).[13] By analogy, these silyl compounds may react with the growing carbon radicals in our living radical polymerization to give end-capped products with similar ketone termini; the polymer end will therefore lack carbon−halogen bonds to be dissociated by the ruthenium complex for further polymerization. In fact, as reported very recently,[14] related silyl enol ethers react with a series of alkyl and arenesulfonyl chlorides in the presence of $RuCl_2(PPh_3)_3$ to produce the corresponding ketones and trimethylsilyl chloride (eq 3). The processes are considered to involve radicals as in our living MMA polymerization (eq 1).



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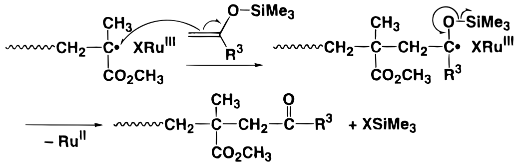

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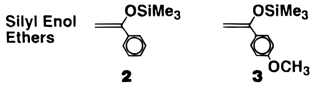


2 **3**

Herein we report that silyl enol ethers, such as α-(trimethylsilyloxy)styrene (**2**) and p-methoxy-α-(tri-

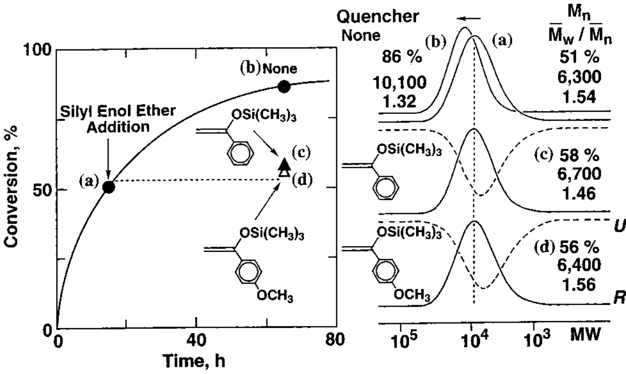


Figure 1. Polymerization of MMA and MWD curves of poly(MMA) obtained with **1**/$RuCl_2(PPh_3)_3$/$Al(OiPr)_3$ in the absence or presence of silyl enol ethers (**2** and **3**) in toluene at 80 °C: $[MMA]_0 = 2.0$ M; $[\mathbf{1}]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(OiPr)_3]_0 = 40$ mM; $[\text{silyl enol ether}]_{add} = 200$ mM. Key: (●) In the absence of silyl enol ether; (▲) addition of **2**; (△) addition of **3**.

methylsilyloxy)styrene (**3**), serve as efficient quenchers in the living radical polymerization of MMA with $RuCl_2(PPh_3)_3$ complex to produce ketone-capped polymers that are interesting end-functionalized polymers and also permit quantitative termination of the growing species.

Results and Discussion. (a) Quenching of Living Radical Polymerization of MMA. MMA was polymerized with a binary initiating system consisting of dimethyl 2-chloro-2,4,4-trimethylglutarate [$(MMA)_2$−Cl, **1**; initiator][15] and $RuCl_2(PPh_3)_3$ in the presence of aluminum triisopropoxide [$Al(OiPr)_3$] in toluene at 80 °C.[16,17] The initiator **1** is the authentic dimer of MMA capped with a chlorine and thus regarded as a model compound of the dormant PMMA to be generated in the ruthenium complex-mediated living radical polymerization with the halogen-capped dormant species (−C−X).

When monomer conversion reached ca. 50%, the two silyl enol ethers (**2** and **3**), 10 mol equiv to **1**, were added to the reaction mixtures. As shown in Figure 1, no further polymerization occurred in these enolate-added systems in the following 50 h, during which period smooth living polymerization proceeded to near 100% conversion in the control runs without quenchers. Thus, both silyl enol ethers (**2** and **3**) efficiently terminate the ruthenium-mediated living radical polymerization.

Figure 1 also compares the molecular weight distributions (MWDs) of polymers obtained with and without silyl enolate quenching, as observed by size-exclusion chromatography (SEC) under refractive index (RI) and ultraviolet (UV; at 254 nm) detections. The poly(MMA) in the controlled runs (SEC traces a and b) were nearly transparent toward UV light, and their MWDs under RI detection were fairly narrow and shifted toward high molecular weights as conversion increased from 51% to 86%. The number-average molecular weight (M_n) by SEC (PMMA calibration)[17] thus increased in direct proportion to conversion.

On the other hand, such an increase in polymer molecular weight stopped on addition of the quenchers. In accordance with the virtual absence of conversion increase, the samples obtained after quencher addition (SEC traces c and d, Figure 1) gave MWD traces (RI detection) that are nearly the same in position, shape, and narrowness as that (trace a) for the control run immediately before the quencher addition; M_n values by SEC were also close among these three samples. Namely, the termination by the silyl enol ether is efficient and fast enough, relative to the propagation, to prevent MWD broadening during the reaction with the growing ends.

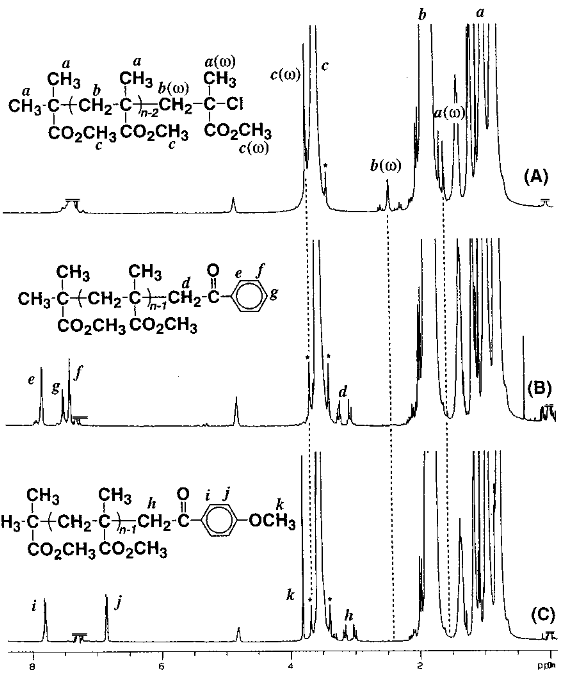


Figure 2. ^1H NMR spectra of poly(MMA) obtained with **1**/$RuCl_2(PPh_3)_3$/$Al(OiPr)_3$ in the absence or presence of silyl enol ethers (**2** and **3**) in toluene at 80 °C. The lines marked by * are ascribed to satellite lines.

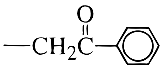
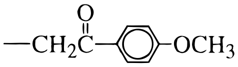
As seen in the broken-line SEC traces, in addition, the quenched samples [(c) and (d)] were UV active at 254 nm. The UV traces extended over the entire range of molecular weight detected by RI (traces in straight line) and were similar in shape to the corresponding RI traces, though the peak molecular weights were different (lower for the UV trace).

These dual mode SEC analyses, therefore, not only support the efficient termination but also indicate that strong UV chromophores are attached to the quenched polymers in the entire range of their molecular weight; most likely, the chromophore is the conjugated aromatic ketone [$R-C_6H_4-CO-$; R = H or (p-)CH_3O; cf. eq 3] derived from the silyl enolate quenchers.

(b) End-Group Analysis. The end-group structures of the polymers thus obtained with and without the quenchers were analyzed by ^1H NMR spectroscopy (Figure 2).[18] The control sample (A) for the quencher-free system exhibits the characteristic signals of the poly(MMA) main chain and the terminal MMA unit capped with an ω-end chlorine: i.e., fairly sharp signals at 2.5 ppm [peak b(ω)] for the methylene protons and at 3.8 ppm [peak c(ω)] for the methoxy protons. As determined from the signal intensity ratio of the terminal methylene [b(ω)] to the ester methyl protons [c] of the main chain, the DP_n(NMR) of this polymer agrees with that by SEC [DP_n(SEC); Table 1]. The number-average end functionality (F_n) of the chlorine end was also determined from the ratio DP_n(SEC)/DP_n(NMR). The value was close to unity, indicating that all polymer chains have chlorine ends.

Polymers B and C, quenched with **2** and **3**, respectively, were virtually free from signals b(ω) and c(ω) for the chlorine terminal but exhibited new absorptions related to the quenchers, i.e., (B) signals d−g with **2**

Table 1. $\overline{DP}_n$ and $\bar{F}_n$ of Poly(MMA) Quenchers with Silyl Enol Ethers[a]

	$\overline{DP}_n$		
ω–end	SEC[b]	NMR[c]	$\bar{F}_n$[d]
—Cl (Control)	65.1	58.8	1.11
	70.2	72.4	0.97
	67.6	69.1	0.98

[a] $[\mathrm{MMA}]_0 = 2.0$ M; $[(\mathrm{MMA})_2{-}\mathrm{Cl}]_0 = 20$ mM; $[\mathrm{RuCl_2(PPh_3)_3}]_0 = 10$ mM; $[\mathrm{Al(O}i\mathrm{Pr)_3}]_0 = 40$ mM; $[\mathrm{quencher}]_{\mathrm{add}} = 200$ mM; in toluene at 80 °C. [b] $[M_n(\mathrm{SEC}) - \mathrm{MW}(\omega\text{-end moiety})]/\mathrm{MW(MMA)}$. [c] From ^{1}H NMR peak intensity ratio; $2[c + c(\omega)]/3b(\omega)$ [Cl], $5c/3(e + f + g)$ $[\mathrm{CH_2C(O)C_6H5}]$, $4c/3(i + j)$ $[\mathrm{CH_2C(O)}\text{-}p\text{-}\mathrm{CH_3O{-}C_6H_4}]$. See Figure 2. [d] $\overline{DP}_n(\mathrm{SEC})/\overline{DP}_n(\mathrm{NMR})$.

and (C) signals h−k with **3**. The upfield signals d and h, both pairs of doublets, are assignable to the methylene group that connects the MMA main chain and the terminal ketone. The downfield sets of multiplets e−f and i−j obviously originate from the aromatic rings of silyl enol ethers **2** and **3**, respectively. No absorptions indicative of other terminal groups were detected.

The observed terminal signals further gave DP_n's and end functionalities F_n's for the quenched polymers (Table 1). The DP_n(NMR) was determined from the signal intensity ratio of the aromatic protons [(e)−(f) or (i)−(j)] to the methoxy protons (c) of the main chain; the F_n was determined from the ratio DP_n(SEC)/DP_n(NMR). The DP_n's by NMR and by SEC are in good agreement with each other, and thus the F_n's are very close to unity, indicating the quantitative attachment of these silyl enol ethers to the polymer ends.

Mechanistically, the quantitative ketone attachment is of interest, in relation to the dynamic equilibrium between covalent (dormant) and radical (active) growing species (eq 3) where the former predominates the latter. To account for the results, obviously, the silyl enol ethers should react with both the dormant and the radical species, or they can react with the radical species only, but the quenching reaction, as well as the dissociation of the dormant end, is fast enough relative to propagation that the radical species are efficiently supplied from the reservoir of the dormant species by the ruthenium-assisted dissociation, while the radical ends are parallely annihilated by silyl enol ethers. This open question is now being examined by us.[19]

In conclusion, silyl enol ethers **2** and **3** have been shown to be efficient quenchers (end-capping agents) that fulfill all criteria discussed in the Introduction. Namely, in-situ addition of the silyl enol ethers quantitatively terminated the ruthenium-mediated living radical polymerization of MMA to give polymers whose ω-ends are cleanly capped with an aromatic ketone to be suitable for quantification of the polymer concentration.

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(15) The initiator **1** was synthesized as follows: Dimethyl 2,2,4-trimethylglutarate (7.80 g, 38.6 mmol)[20] was added to a stirred solution of lithium diisopropylamide (40 mmol) in hexane/THF mixed solution at −78 °C under dry nitrogen. The mixture was stirred for 2 h, and carbon tetrachloride (7.38 g, 48 mmol) was added dropwise over a period of 5 min at −78 °C. The mixture was slowly allowed to warm to room temperature and stirred for an additional 2 h. The resultant solution was evaporated under reduced pressure, diluted with ether (100 mL) and treated with water. The aqueous layer was extracted with ether (100 mL). The combined organic phase was washed three times with 1 N hydrochloric acid (100 mL each) and then three times with deionized water (100 mL each), dried over anhydrous sodium sulfate overnight, and evaporated under reduced pressure to give the chloro ester **1**, which was purified by recrystallization from hexane (four times): ^{1}H NMR (500.16 MHz, CDCl$_3$) δ 1.16 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.71 (s, 3H, CH_3), 2.56 (m, 2H, CH_2), 3.68 (s, 3H, CO$_2$CH_3), 3.78 (s, 3H, CO$_2$CH_3); ^{13}C NMR (67.94 MHz, CDCl$_3$) δ 25.4, 25.6, 28.4, 41.7, 50.3, 51.9, 53.0, 67.1, 171.9, 177.5.

(16) The polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock or in baked and sealed glass tubes. All reagents were used after ordinary purifications, and the toluene solvent was bubbled with dry nitrogen for more than 15 min immediately before use. The polymerization was initiated by adding, via dry syringes, MMA (0.535 mL), *n*-octane (0.100 mL), and solutions of **1** (0.067 mL, 750 mM) and Al(O*i*Pr)$_3$ (0.80 mL, 125 mM) in toluene sequentially, in this order, into a solution of RuCl$_2$(PPh$_3$)$_3$ (1.0 mL, 25 mM) at 25 °C.; thus the total volume of the reaction mixture was 2.5 mL. Immediately after mixing, the mixture was placed in an oil bath kept at 80 °C. After 15 h, a solution of silyl enol ether (**2** or **3**) in

toluene (0.5 mL, 1.0 M) was added into the polymerization solution. After 50 h, the polymerization was terminated by cooling the reaction mixtures to −78 °C. Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography with *n*-octane as an internal standard. 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 Co., Ltd.] (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 vacuum dried overnight.

(17) The M_n, M_w/M_n, and MWD of the polymers were determined by size-exclusion chromatography in chloroform with a calibration based on eleven poly(MMA) standard samples (Polymer Laboratories; $M_n = 630-1200000$; $M_w/M_n = 1.04-1.22$).

(18) ^{1}H NMR spectra (500.16 MHz) were recorded on a JEOL JNM-LA500 in $CDCl_3$ at 27 °C. The samples for ^{1}H NMR analysis were isolated by preparative size-exclusion chromatography (Shodex K-2002; exclusion limit = 5×10^3; 2.5 cm i.d. × 30 cm).

(19) Our preliminary results showed that no reaction occurs between the chloride dormant polymer terminal and the silyl enol ethers in the absence of $RuCl_2(PPh_3)_3$. Tokuchi, K.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **1998**, *47*(7), paper IIPa003.

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