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End-Functionalization with Alcohols in Metal-Catalyzed Living Radical Polymerization through Umpolung of Growing Carbon−Halogen Bond

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ABSTRACT: A novel method is described for the synthesis of end-functionalized polymers [−C−OR; R = CH_2CH_2OH, $(CH_2)_3CH{=}CH_2$; $CH_2C(O)C_6H_5$] via sequential terminal "umpolung" and alkoxy end-capping in metal-catalyzed living radical polymerizations of methyl acrylate and methacrylate with Ru(II) catalysts. The first umpolung step involved the single-unit addition of a "modifier" monomer [$CH_2{=}C(OCH_3)C_6H_5$; αMOS] onto the growing carbon−halogen end (∼∼C−X; X = Cl, Br) to modify it from neutral (radical) into more nucleophilic (carbocationic). Subsequently, the modified terminal was quantitatively end-capped into an alkoxy with a functionalized alcohol (ROH). Systematic evaluation indicated that the "modifier" monomer be bulky (geminally disubstituted) and thus incapable of homopropagation and be electron-rich and conjugated for promoting the subsequent electrophilic substitution of alcohols. Thus, α-methoxystyrene (αMOS) was better suited than its α-monosubstituted *p*-methoxy and α-methyl-*p*-methoxy versions, with which respectively homopropagation overrode the single addition and HX elimination over the alcoholic substitution. For the second step a variety of functionalized alcohols are available; the simple methoxy from methanol may further be reduced into a more versatile ketone functionality. Similarly, telechelic polymers were also obtained from α,ω-bifunctional polymers.

Introduction

End-functionalized polymers are versatile in synthetic applications such as surface modification, sealing (as sealants), block copolymer synthesis, and, most recently, bioconjugation.[1] They are usually prepared by living polymerization, either by initiation or by end-capping, or both (into telechelics). Functionalized initiators and terminators (end-capping agents) have thus been developed, but in living radical polymerization, the neutrality of intermediate radicals renders quantitative end-capping relatively difficult, with the scope of end-cappers thus limited. This problem is especially true for metal-catalyzed systems involving dormant species where the carbon−halogen terminal is covalent, highly stable, less polarized, and thereby less suitable for end-capping via substitution.[2] To date, few methods have been reported for radical end-capping: silyl enol ethers for ketones,[3] tin compounds for hydrogenation and allylation,[4] allyl compounds for hydroxyl and epoxide groups,[4b,5] and sodium azides for "click" reactions;[6] and these are not free from problems and limitations in terms of readily available end-functionality and sometimes safety.

We have recently developed a versatile end-capping method to quantitatively convert a dormant halogen terminal into other functional groups in the metal-catalyzed living radical polymerization of methyl methacrylate (MMA),[7] in which the rather unreactive −MMA−Cl terminal may be converted into an electrophilically more reactive −MMA−(alkoxystyrene)−Cl end (Scheme 1).[8] The crucial point is *umpolung*[9] of the terminal carbon−halogen bond via the addition of a "modifier monomer", such as *p*-methoxystyrene (pMOS) or α-methoxystyrene (αMOS), that carries a highly electron-donating as well as conjugating pendent group. Thus, the α-substituent adjacent to the terminal carbon−halogen linkage is converted in situ from electron-withdrawing into electron-donating so as to be accessible to nucleophilic reagents; most typically, an MMA ester into an αMOS alkoxyphenyl for alcohol end-capping into an alkoxy (acetal) terminal. Obviously, the design criteria for the modifier monomer involve the selection of an ambivalent umpolung group, as with the *p*- or α-alkoxyphenyl group, that is conjugating for radical addition and electron-donating for the subsequest nucleophilic substitution.

In this paper, we examined the utility and scope of this umpolung end-capping methodology for the ruthenium(II)-catalyzed living radical polymerization (Scheme 2). We first employed various monomers as potential *umpolung* end-group modifiers to examine the effects of their structure on this end-functionalization. Second, we employed various functionalized alcohols for synthetically attractive end-functionalization. As a result, a nonconjugated olefin and a hydroxy group were quantitatively introduced onto the poly(MMA) terminal through the sequential addition of αMOS (modifier) and a functionalized alcohol (i.e., 4-penten-1-ol and ethylene glycol, respectively). A ketone terminal was also obtained from the acetal derivative, derived from the αMOS/methanol combination, via a simple acid treatment.

Experimental Section

Materials. MMA (Tokyo Kasei; purity >99%), methyl acrylate (MA, Tokyo Kasei; >99%), and styrene (St, Wako; >99%) were dried overnight over calcium chloride and distilled twice from calcium hydride under reduced pressure before use. Ethyl 2-chloro-2-phenylacetate (ECPA, Aldrich; >97%) and ethyl 2-bromoisobutyrate (H-EMA-Br, Tokyo Kasei; >98%) were distilled under reduced pressure before use. 2,2-Dichloroacetophenone (Aldrich; 97%) was distilled from calcium hydride under reduced pressure before use. $RuCl(Ind)(PPh_3)_2$ (Strem) and $RuCl(Cp^*)(PPh_3)_2$ (Aldrich) were used as received and handled in a glovebox under a moisture- and oxygen-free argon atmosphere (H_2O < 1 ppm, O_2 < 1 ppm). *n*-Octane (internal standard for gas chromatography for MMA) was dried overnight over

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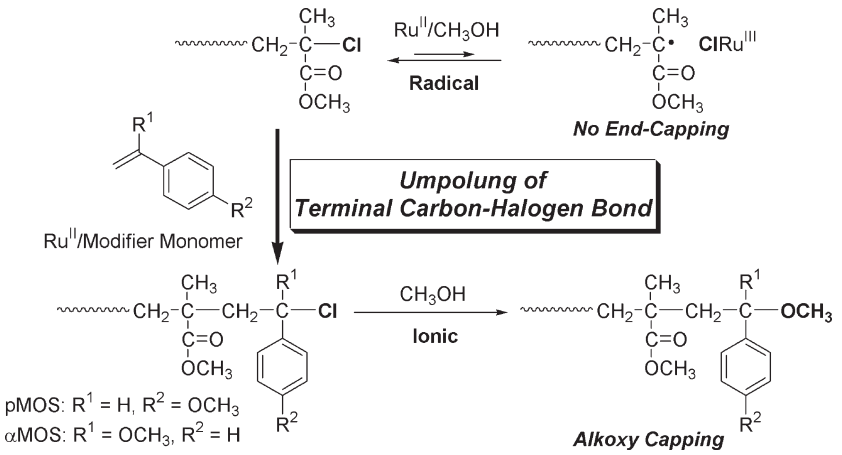
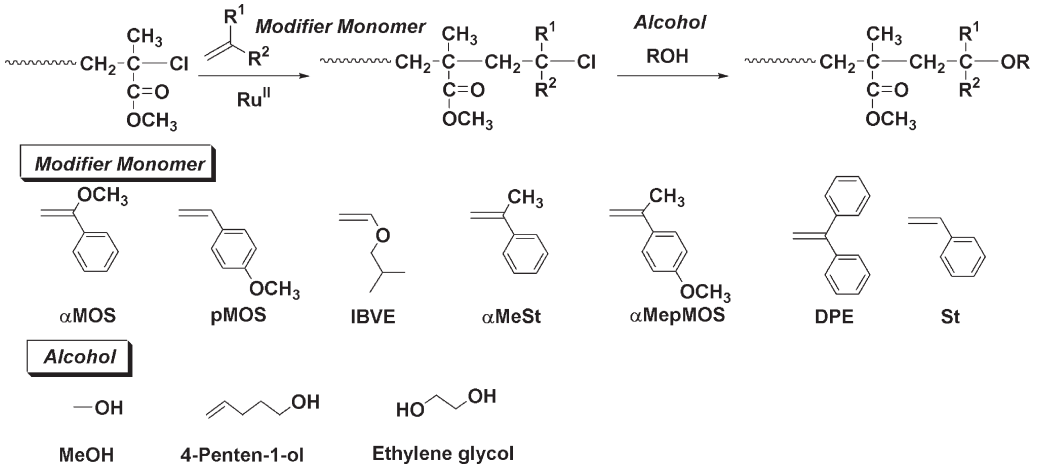
Scheme 1. Umpolung of Terminal Carbon−Halogen Bond with Modifier Monomer



Scheme 2. Umpolung of Terminal Carbon−Halogen Bond toward End-Functionalization



calcium chloride and purified by double distillation from calcium hydride before use. Methanol (MeOH, Wako; dehydrated), 4-penten-1-ol (Aldrich; 99%), ethylene glycol (Aldrich; anhydrous, 99.8%), and *n*-Bu_3N (Tokyo Kasei; >99%) was bubbled with dry nitrogen for more than 15 min before use. Toluene (solvent) was passed through purification column (solvent dispensing system; glass contour) before use. *p*-Methoxystyrene (pMOS, Aldrich; >97%) and α-methylstyrene (αMeSt, Tokyo Kasei; >99%) were washed with 10% aqueous sodium hydroxide and then with saturated aqueous sodium chloride, dried overnight over sodium sulfate, and distilled under reduced pressure before use. α-Methoxystyrene (αMOS)[10] and α-methyl-*p*-methoxystyrene (αMepMOS)[11] were prepared according to the literature. Isobutyl vinyl ether (IBVE, Tokyo Kasei; >99%) was washed with 10% aqueous sodium hydroxide and then with water, dried overnight over potassium hydroxide, and distilled twice from calcium hydride before use. 1,1-Diphenylethylene (DPE, Wako; >95%) was dried overnight over sodium sulfate and distilled under reduced pressure before use.

Polymerization and End-Capping Reaction. The polymerization was carried out by the syringe technique under dry argon in baked glass tubes equipped with a three-way stopcock. A typical procedure is given below for an acetal-capped poly(MMA) (Scheme 2; R^1 = OMe, $R^2 = C_6H_4OMe$), namely, the polymerization of MMA with ECPA/RuCl(Ind)$(PPh_3)_2$/*n*-Bu_3N and the subsequent sequential end-capping reaction with αMOS and then methanol: In an argon-filled glass tube was placed RuCl(Ind)$(PPh_3)_2$ (0.01 mmol, 7.76 mg), to which toluene (3.45 mL), *n*-octane (0.13 mL), *n*-Bu_3N (0.25 mL, as a 400 mM solution in toluene, 0.1 mmol), MMA (1.07 mL, 10 mmol), and ECPA (0.10 mL, as a 995.8 mM solution in toluene, 0.1 mmol) were added sequentially in this order at room temperature under dry argon. The total volume of the reaction mixture was thus 5.0 mL. Immediately after mixing, the mixture was placed in an oil bath kept at 80 °C for 13 h. The polymerization solution was evaporated under reduced pressure under an inert and air-free atmosphere to remove the residual monomer. Toluene (4.21 mL), *n*-Bu_3N (0.25 mL, as a 400 mM solution in toluene, 0.1 mmol), methanol (0.41 mL, 10 mmol), and αMOS (0.13 mL, 1.0 mmol) were added sequentially, and the mixture was placed again in an oil bath kept at 80 °C. In predetermined intervals, aliquots of the solution were sampled out and terminated by cooling to −78 °C to monitor the progress of the reaction. 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 evaporated to dryness to give the products, which were subsequently vacuum-dried overnight.

Transformation of Acetal Terminal into Ketone. An acid solution, 1.0 M HCl_{aq} (0.07 mL) was added to a $CHCl_3$ solution of the acetal-capped polymer (0.03 g, 0.6 mL), and the mixture was stirred at room temperature for 24 h. The solution was evaporated to dryness to give the ketone-capped product, −MMA−C(C_6H_4OMe)═O.

Measurements. The M_n, M_w/M_n, and molecular weight distribution (MWD) of the polymers were determined by size-exclusion chromatography (SEC) in chloroform at 40 °C using three polystyrene gel columns [Shodex K-805 L (pore size: 20−1000 Å; 8.0 mm i.d. × 30 cm) × 3; flow rate 1.0 mL/min] that were connected to a Jasco PU-980 precision pump, a Jasco RI-930 refractive index detector, and a Jasco UV/vis detector set at 250 nm. The columns

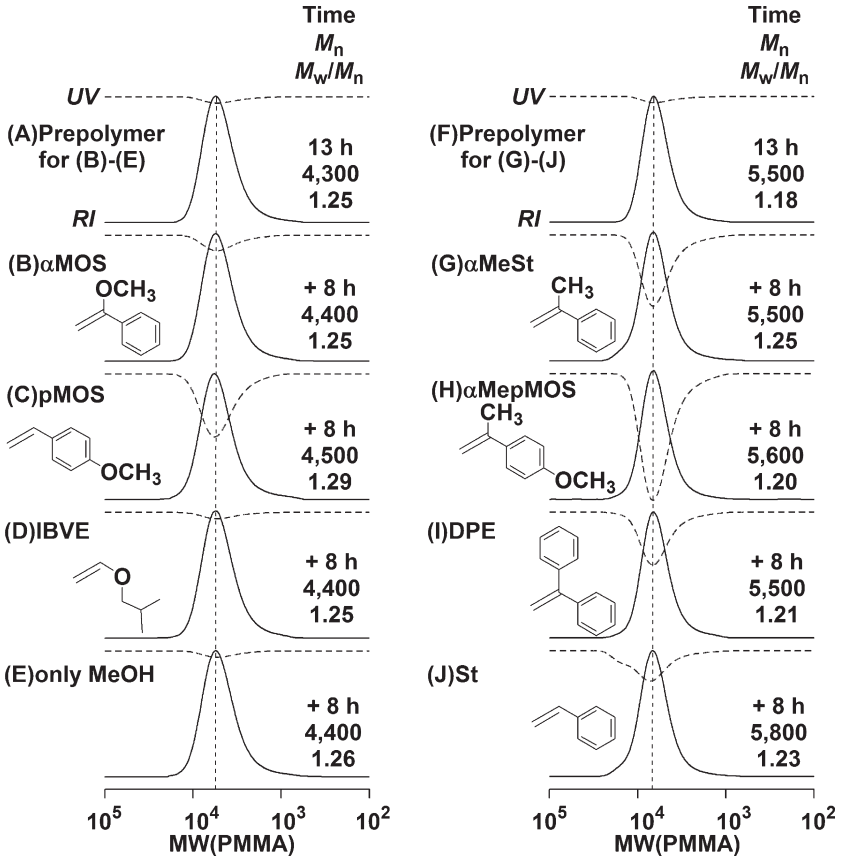


Figure 1. SEC curves of PMMAs obtained with ruthenium-catalyzed living radical polymerization (samples A and F) and subsequent sequential end-capping reactions with a modifier monomer and methanol in toluene at 80 °C (samples B−E from the prepolymer A and samples G−J from F). Polymerization conditions for samples A and F: $[MMA]_0 = 2.0$ M; $[ECPA]_0 = 20$ mM; $[Ru(Ind)Cl(PPh_3)_2]_0 = 2.0$ mM; $[n\text{-}Bu_3N]_0 = 20$ mM; for 13 h; conversion 30−40%.[15] End-capping reactions for samples B−E and G−J: $[\text{modifier monomer}]_{add} = 200$ mM; $[MeOH]_{add} = 2.0$ M; $[n\text{-}Bu_3N]_{add} = 20$ mM (additionally applied upon the modifier addition); modifier addition at 13 h; end-capping for an additional 8 h. Modifier: (B) αMOS; (C) pMOS; (D) IBVE; (E) none (control experiment); (G) αMeSt; (H) αMepMOS; (I) DPE; (J) St.

were calibrated against 12 standard poly(MMA) samples (Polymer Laboratories; $M_n = 630-1\,200\,000$; $M_w/M_n = 1.06-1.22$) as well as the monomer. ^{1}H NMR spectra were recorded in $CDCl_3$ at room temperature on a JEOL JNM-LA500 spectrometer, operating at 500.16 MHz. Polymer samples for ^{1}H NMR were fractionated by preparative SEC (column: Shodex K-5002F). MALDI-TOF-MS analysis was performed on a Shimadzu AXIMA-CFR instrument equipped with 1.2 m linear flight tubes and a 337 nm nitrogen laser.

Results and Discussion

Design of Modifier Monomers. We examined a series of vinyl compounds as potential modifier monomers for the ruthenium-catalyzed living radical polymerization of MMA, followed by end-capping with methanol. As discussed in the Introduction, the selection criteria included (a) the quantitative and possibly single-unit addition to the living poly(MMA) end and (b) the fast and quantitative termination with methanol to give a methoxy-capped polymer. Two samples of prepolymers were first prepared by the MMA polymerizations with a ruthenium catalyst $[RuCl(Ind)(PPh_3)_2$, Ind = η^5-$C_9H_7]$,[12] in conjunction with a chloride initiator (ECPA)[13] and an amine cocatalyst (n-Bu_3N)[14] in toluene at 80 °C, where conversion reached 30−40% in 13 h (Figure 1, A and F). For both samples, the terminal group was chlorine (Cl) with an almost quantitative functionality [$F_n(\omega) > 0.95$ by ^{1}H NMR], indicating the polymerizations were well controlled.[15]

The polymerization solutions were then evaporated under an inert and air-free atmosphere to remove the remaining MMA. To the as-obtained residues were added, sequentially, an excess of a modifier monomer (10 mol equiv to the prepolymer), excess methanol (100 equiv), n-Bu_3N (to be 40 mM after addition), and toluene, and the solution was heated and kept at 80 °C for an additional 8 h. The resultant polymers were analyzed by SEC (with RI and UV detectors, Figure 1), MALDI-TOF-MS (Figure 2), and ^{1}H NMR.[7] As already reported, the reactions with αMOS or pMOS induced a quantitative methoxy-capping (B and C, respectively, both in Figures 1 and 2; $F_{n,\,methoxy} > 0.98$ by ^{1}H NMR).[7] With the α- or p-methoxy substituent, the electron-rich and highly reactive radical species derived from these modifiers thus led to the effective cationic end-capping with the methoxy group from added methanol. Note that the quantitative and selective single-unit addition took place with αMOS, whereas the addition was multiple with pMOS; thus, the former is among the best end-group modifiers (see below).

In contrast, few end-capping reactions occurred with isobutyl vinyl ether (IBVE) (D in both Figures 1 and 2; $F_{n,methoxy} \sim 0.15$ by ^{1}H NMR), most likely because IBVE is indeed electron-donating but nonconjugating ($e = -1.27$; $Q = 0.030$) and thus inefficient in radical addition.[16] With α-methylstyrene derivatives (i.e., αMeSt and αMepMOS), both electron-donating and conjugating, therefore, the expected addition did proceed, as indicated by the SEC curves of the products where the UV response (250 nm) sharply increased while peak positions little shifted (Figure 1, G and H). However, MALDI-TOF-MS and ^{1}H NMR analysis revealed that the main terminals were not the expected methoxy

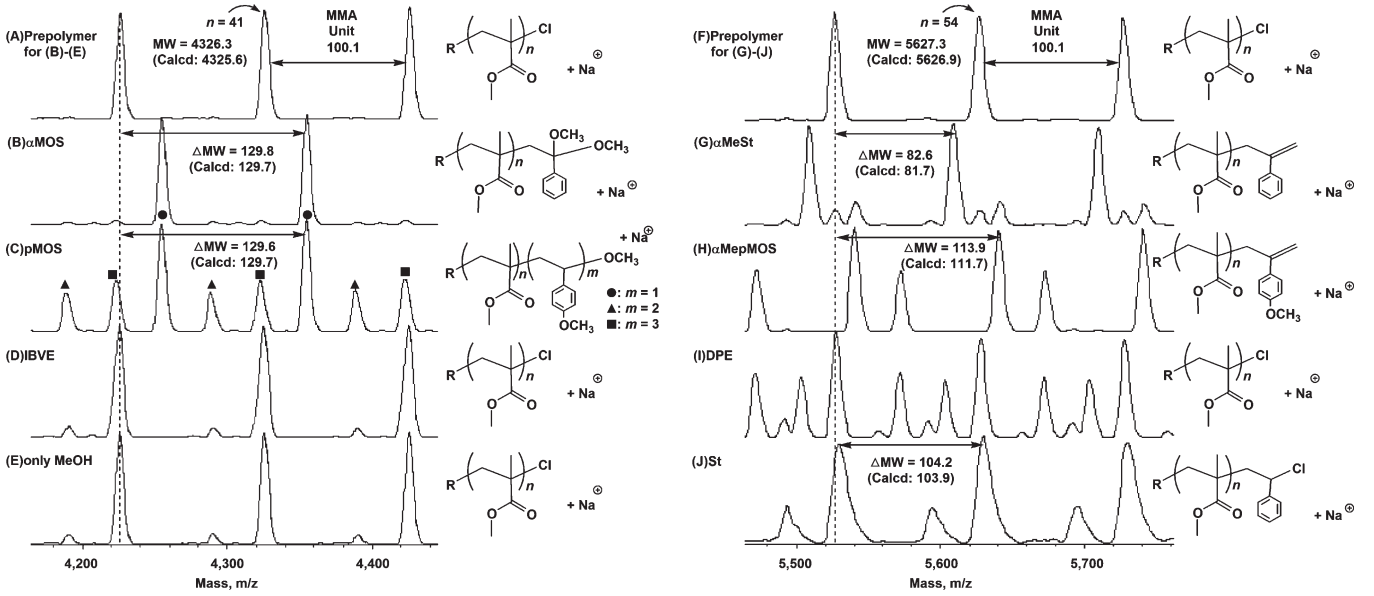


Figure 2. MALDI-TOF-MS spectra of PMMAs. See Figure 1 for the reaction conditions. The chemical drawings represent polymer structures characterized by masses of series peaks (only main products).

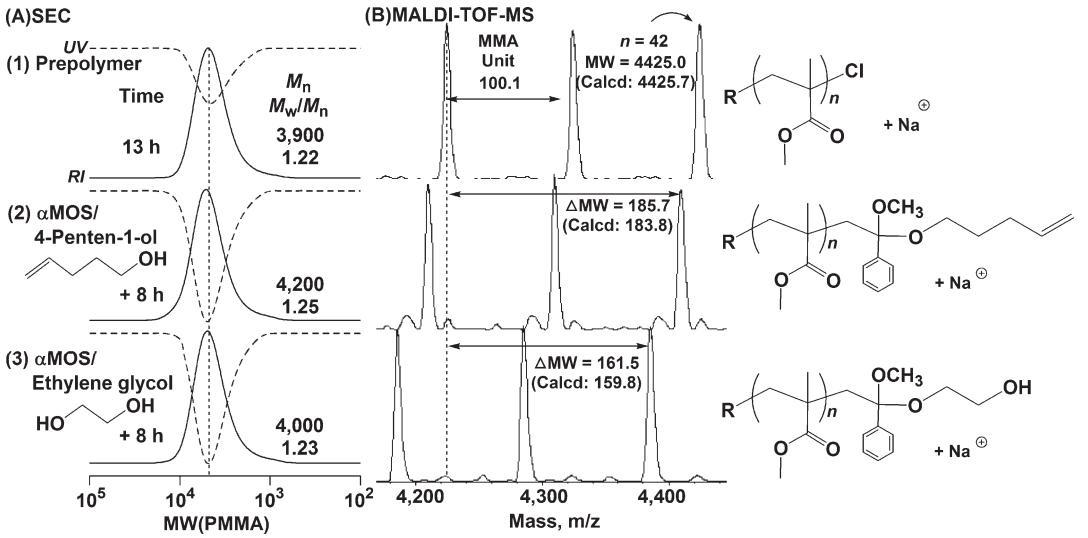


Figure 3. Structural analyses with (A) SEC curves and (B) MALDI-TOF-MS spectra for end-functionalization using 4-penten-1-ol (olefin) and ethylene glycol (hydroxyl). (1) Prepolymer PMMA (polymerization in 13 h). (2) End-capping with αMOS and 4-penten-1-ol. (3) End-capping with αMOS and ethylene glycol. Polymerization: $[MMA]_0 = 2.0$ M; $[ECPA]_0 = 20$ mM; $[Ru(Ind)Cl(PPh_3)_2]_0 = 2.0$ mM; $[n\text{-}Bu_3N]_0 = 20$ mM. End-capping reaction: $[\alpha MOS]_{add} = 200$ mM; $[alcohol]_{add} = 2.0$ M; $[n\text{-}Bu_3N]_{add} = 20$ mM. Reaction time for end-capping is 8 h.

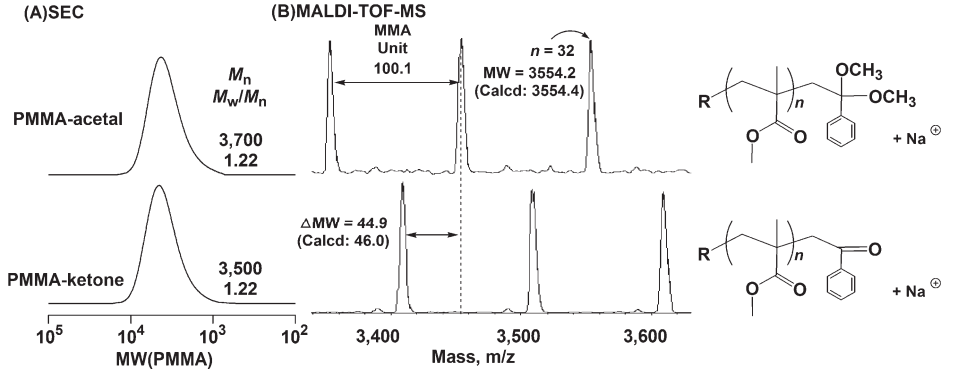
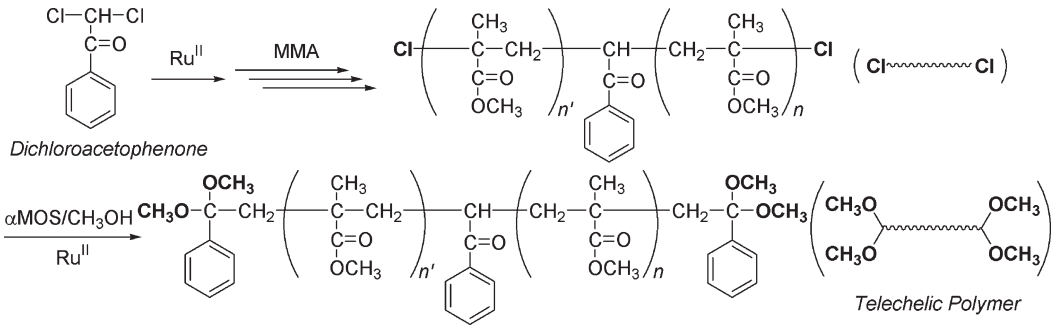


Figure 4. Structural analyses with (A) SEC curves and (B) MALDI-TOF-MS spectra for terminal conversion from acetal (PMMA−acetal: upper) to ketone (PMMA−ketone: lower) by the acidic treatment. See Figure 1 for the MMA polymerization with the ruthenium catalyst and the end-capping reaction with αMOS and methanol. Conversion from acetal to ketone: PMMA−acetal = 0.008 mmol in $CHCl_3/HCl_{aq}$ (9/1, v/v) at rt for 24 h, followed by evaporation.

Scheme 3. Synthesis of Telechelic PMMA with Bifunctional Initiator



by methanol-quenching [$F_{n,methoxy} \sim 0.06$ (αMeSt), 0.34 (αMepMOS) by ^{1}H NMR] but an exo-olefin by the proton elimination from the terminal α-methyl (Figure 2, G and H). These monomers indeed added radically to the PMMA terminal, but the resulting terminals seemed so unstable that, upon treatment with methanol, HCl elimination occurred in preference to methoxy capping.[3b,17]

In consideration of these facts, 1,1-diphenylethylene (DPE) was employed, which is geminally α-disubstituted but would be immune to such elimination. However, DPE almost failed to add onto the PMMA terminal, and the main series of MALDI-TOF-MS peaks was identical to that of the precursor (Figure 2I; $F_{n,methoxy} \sim 0.27$ by ^{1}H NMR). With styrene, a monosubstituted version of DPE, on the other hand, the SEC profile consisted of not only an enhanced UV peak but also an additional shoulder in the higher molecular weight region (Figure 1J). This would indicate that a styrene unit was introduced at the poly(MMA) terminal, but a small part of the resultant less stable styryl radical would have undergone bimolecular radical coupling. Also, the terminal turned out to be primarily a Cl-capped styrene unit, according to MALDI-TOF-MS analysis, and thus no methoxy group was introduced at all. Presumably, the electron donacity of the styrene's phenyl group ($e = -0.80$) is not high enough for the ionic substitution with methanol.[16]

From these results, pMOS and αMOS proved to be suitable as a modifier monomer for poly(MMA), and especially αMOS gives well-defined end structures consisting of one unit of αMOS capped with a methoxy group.[7] Furthermore, theses results verify the proposed umpolung mechanism (Scheme 2) with the modifier monomers, electron-donating, conjugating, and free from proton elimination or other side reactions.

End-Functionalized Polymers. *a. Olefin and Hydroxyl Groups.* For the end-capping after the umpolung, a variety of alcohols were employed in place of methanol to introduce a functional group at the terminal, coupled with αMOS as a modifier monomer. For an olefin or a hydroxyl terminal, 4-penten-1-ol or ethylene glycol, respectively, together with αMOS was added into a solution of living PMMA at a ca. 40% conversion, and the mixtures were stirred for 8 h; just prior to alcohol addition, the remaining MMA monomer was removed by evaporation.[7] The resultant polymers were then characterized by SEC and MALDI-TOF-MS (Figure 3). With both alcohols, the products showed SEC-RI traces just slightly shifting toward high MW region with narrow MWDs ($M_w/M_n < 1.25$), and intensified UV responses indicated the attachment of terminal αMOS units. MALDI analysis clearly demonstrated

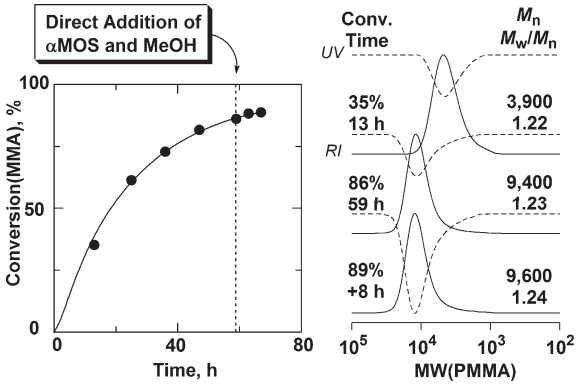


Figure 6. Time−conversion curve and SEC curves for direct end-capping reaction with αMOS/methanol for ruthenium-catalyzed living radical polymerization of MMA. Polymerization: $[MMA]_0 = 2.0$ M; $[ECPA]_0 = 20$ mM; $[Ru(Ind)Cl(PPh_3)_2]_0 = 2.0$ mM; $[n\text{-}Bu_3N]_0 = 20$ mM. αMOS and methanol were added at 86% conversion: $[\alpha MOS]_{add} = 200$ mM; $[MeOH]_{add} = 2.0$ M. Reaction time for end-capping is an additional 8 h.

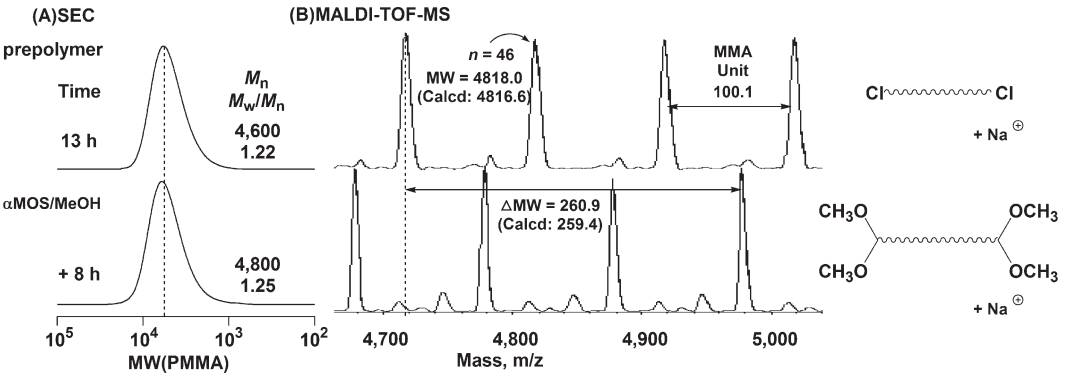


Figure 5. Structural analyses with (A) SEC curves and (B) MALDI-TOF-MS spectra for end-capping reaction of telechelic PMMA obtained with a bifunctional initiator under the ruthenium catalysis. Polymerization: $[MMA]_0 = 2.0$ M; [2,2-dichloroacetophenone]$_0 = 20$ mM; $[Ru(Ind)Cl(PPh_3)_2]_0 = 2.0$ mM; $[n\text{-}Bu_3N]_0 = 20$ mM in toluene at 80 °C. Polymerization time is 13 h (conversion: 51%). End-capping reaction: $[\alpha MOS]_{add} = 400$ mM; $[MeOH]_{add} = 4.0$ M; $[n\text{-}Bu_3N]_{add} = 40$ mM. Reaction time for end-capping is 8 h.

almost quantitative introduction of the added alcohol (alkoxy) residues carrying an olefin or a hydroxyl group beyond a single unit of αMOS ($F_{n,alkoxy} > 0.90$ by ^{1}H NMR).

b. Ketone. The acetal terminal derived from our umpolung and end-capping with αMOS and methanol may also be converted into a ketone, another highly versatile terminal reactive enough for further functionalization or conjugation with other molecules. For example, upon simple acid treatment (Figure 4), the SEC curve of the resultant polymer was almost the same as that of the pristine sample, while all the MALDI peaks shifted to lower mass by $m/z \sim 46$, in consistent with the quantitative conversion of the acetal to the corresponding ketone [$-CH_2-C(C_6H_5)(OCH_3)_2 \rightarrow -CH_2-C(C_6H_5)=O$]. Note that the acid treatment was carried out under so mild conditions that no side reactions occurred, such as degradation of the PMMA pendent esters.

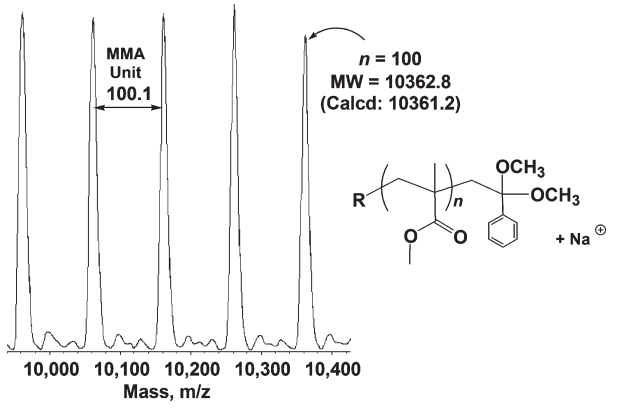


Figure 7. MALDI-TOF-MS spectrum of obtained PMMA in direct end-capping reaction with αMOS/methanol for ruthenium-catalyzed living radical polymerization of MMA. See Figure 6 for the conditions.

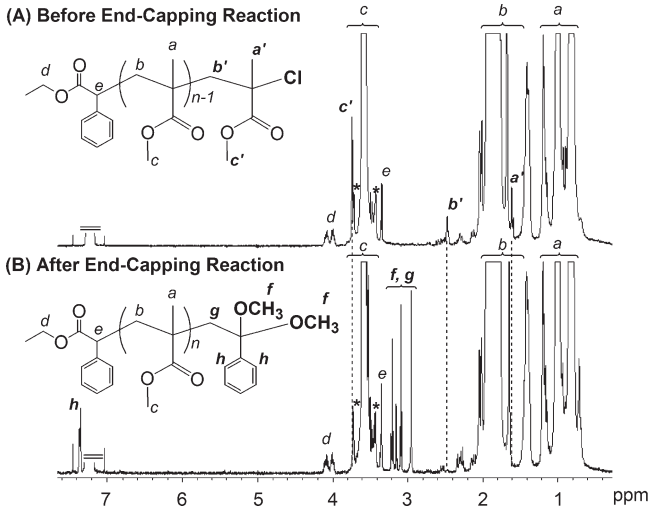


Figure 8. ^{1}H NMR analyses of obtained PMMAs in direct end-capping reaction with αMOS/methanol for ruthenium-catalyzed living radical polymerization of MMA. The asterisks (*) indicate satellite peaks. (A) Before the addition of αMOS/methanol. (B) After the addition. See Figure 6 for the conditions.

Telechelic Polymers. When combined with a bifunctional initiator, 2,2-dichloroacetophenone,[18] the αMOS/methanol end-capping led to telechelic polymers with methoxy (acetal) terminals (Scheme 3). The produced PMMAs were well controlled before and after the capping treatment ($M_w/M_n = 1.22$ and 1.25, respectively), and MALDI (Figure 5) and ^{1}H NMR (Figure S1) analysis verified the desired telechelic architecture, with an average end-functionality ~1.90 (see Supporting Information Figure 1).

Direct Addition of Modifier Monomer and Alcohol without Residual MMA Removal. In the above-described procedures, residual MMA (ca. 40% conversion) should be removed by evaporation prior to the addition of the modifier monomer and an alcohol to ensure the quantitative end-capping. Here, a direct umpolung and end-capping without the evaporation procedure was tested for a simpler and more practically feasible process.

MMA was polymerized with the Ru(Ind)Cl(PPh_3)$_2$-catalyzed system (with ECPA and *n*-Bu_3N) in toluene at 80 °C.[7] When conversion reached as high as around 90%, 10 equiv (for the initiator) of αMOS and 100 equiv of MeOH were directly added to the polymerization mixture (Figure 6). During the reaction for an additional 8 h, MMA conversion had hardly increased, and the desired capping reaction apparently proceeded. Namely, little change was detected in SEC molecular weights and MWD, with enhancement of the UV response, and the quantitative methoxy capping was confirmed by MALDI-TOF-MS (Figure 7) and ^{1}H NMR (Figure 8; $F_{n,methoxy} > 0.94$). The observed MALDI peak masses fairly agreed with that of the expected PMMA with a single unit of αMOS and methoxy. The original NMR peaks from the Cl terminal disappeared: methyl (*d′*, 1.6 ppm), methylene (*b′*, 2.4 ppm), and methoxy (*c′*, 3.7 ppm)]; instead, new peaks from the methoxy terminal appeared: methoxy and methylene (*f* and *g*, 2.9−3.4 ppm) and aromatic (*h*, 7.4 ppm).

Thus, the direct end-capping at the later stage of polymerization was found to be effective, clean, and in particular simpler without an additional MMA removal. Note that this method cannot be available unless the polymerization is precisely controlled even at high monomer conversion.

Versatility: Scope of Monomers. Finally, we applied the alkoxy end-capping methodology for monomers other than MMA, such as methyl acrylate (MA) and styrene (St). For these less reactive monomers, initiator/catalyst combinations were accordingly modified to be best fit for their respective living radical polymerizations: H−EMA−Br/RuCl(Cp*)-(PPh_3)$_2$ for MA[19] and H−EMA−Br/RuCl(Ind)(PPh_3)$_2$ for styrene.[12] As with MMA, when monomer conversion reached 40−50%, residual monomers were removed by evaporation before addition of αMOS and methanol. At this point the polymers from MA and styrene were well controlled and of narrow MWDs ($M_w/M_n \sim 1.2$).

Table 1. Alkoxy End-Capping Reaction for Various Polymers with αMOS and MeOH[a]

			before reaction		after reaction		
monomer	initiator	catalyst	M_n	M_w/M_n	M_n	M_w/M_n	alkoxy end functionality[b]
MMA	ECPA	Ru(Ind)Cl(PPh_3)$_2$	4300	1.25	4400	1.25	0.98
MA	H-EMA-Br	Ru(Cp*)Cl(PPh_3)$_2$	4900	1.18	4900	1.18	0.92
St	H-EMA-Br	Ru(Ind)Cl(PPh_3)$_2$	5200	1.20	5300	1.20	0

[a] Polymerization: $[monomer]_0 = 2.0$ M; $[initiator]_0 = 20$ mM; $[catalyst]_0 = 2.0$ mM; $[n\text{-}Bu_3N]_0 = 20$ mM in toluene at 80 °C for 13 h (MA), at 80 °C for 15 h (MA), or at 100 °C for 24 h (St). End-capping reaction: $[\alpha MOS]_{add} = 200$ mM; $[MeOH]_{add} = 2.0$ M; $[n\text{-}Bu_3N]_{add} = 20$ mM in toluene at 80 °C for 8 h. [b] Determined by ^{1}H NMR.

Table 1 summarizes the structural characterizations of the resultant polymers after the umpolung and end-capping. For MA, the methoxy group was almost quantitatively introduced via one unit of αMOS without side reactions ($F_n \sim 0.92$ by ^{1}H NMR). For styrene, in contrast, no methoxy group was detected by NMR, indicating neither αMOS nor methanol reacted, probably because of the low reactivity of the styryl radical toward electron-rich αMOS. Further optimization of reaction conditions is under way.

Conclusions

We thus demonstrated the availability of the alkoxy end-capping through "umpolung" of the terminal carbon−halogen bond in metal-catalyzed living radical polymerization of MMA and MA. Single units of selected monomers carrying both conjugating and electron-donating groups, pMOS and αMOS, were added onto the terminals and thereby inverted their polarity, so as to facilitate the subsequent nucleophilic substitution by alcohols. The end-capping method was actually useful to prepare not only end-functionalized polymers with olefin, hydroxyl, and ketone at the terminal but also telechelic polymers. Thus, this way would open the door to precisely control polymeric architectures including their terminals with metal-catalyzed living radical polymerization.

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Supporting Information Available: ^{1}H NMR spectrum of telechelic polymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Though the two prepolymer samples (A and F) were obtained separately but under nominally the same reaction conditions (see the caption for Figure 1), they slightly differed in conversion, molecular weight, and MWD: (A) 33%; M_n = 4300; M_w/M_n = 1.25; (F) 44%; M_n = 5500; M_w/M_n = 1.18. The difference was apparently caused by trivial operational factors, e.g., fluctuation in vessel temperature and/or reagent concentration, but did not affect the subsequent end-capping experiments as described in the text. No further attempt was therefore made for clarifying the causes of the difference.
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