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Multifunctional Initiators for the Ruthenium-Mediated Living Radical Polymerization of Methyl Methacrylate: Di- and Trifunctional Dichloroacetates for Synthesis of Multiarmed Polymers[1]

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ABSTRACT: Bi- and trifunctional dichloroacetates were synthesized from the corresponding multifunctional alcohols or phenols and then employed as multifunctional initiators for the living radical polymerizations of methyl methacrylate mediated by $RuCl_2(PPh_3)_3$ in the presence of aluminum compounds such as $Al(O\textit{i}Pr)_3$ and $Al(acac)_3$ (acac: acetylacetonate). All these systems led to living polymerizations. However, the systems with $Al(O\textit{i}Pr)_3$ involved partial transesterification of the ester units in the initiators, which resulted in the formation of a monofunctional initiator. In contrast, new systems with $Al(acac)_3$ did not induce such transesterification and produced the multiarmed living polymers. ^{1}H NMR analysis showed that polymers obtained with the di- and trifunctional esters possessed almost two and three arms, respectively, along with controlled molecular weights and their narrow distributions.

Introduction

Multiarmed or star polymers have been attracting much interest due to their unique spatial shapes and rheological property. Among a variety of methods thus far reported, living polymerization is most suited for the controlled synthesis of the multiarmed polymers with controlled structure, for which there are primarily three methods: (1) living polymerization with a multifunctional initiator; (2) coupling reaction of linear living polymers with a multifunctional coupling agent; and (3) linking reaction of linear living polymers with a divinyl compound. Among them, methods 1 and 2 can afford predetermined numbers of arms per molecule.

The three approaches have been successfully employed in various living polymerizations including anionic, cationic, and metathesis mechanisms,[2] but few examples are known in radical polymerizations due to the hitherto lack of living systems comparable to the ionic or coordinated counterparts; radical polymerization has been considered difficult to control because of undesirable side reactions, particularly disproportionation and recombination between the polymer terminals, which are prone to neutral radical growing ends.[3] Regardless of such a view, many efforts to achieve living radical polymerization have recently been made.[4] Most of the contemporary living or controlled radical polymerizations involve growing radical species that are temporally stabilized into covalent and dormant species by which fine reaction control is realized, and some of them in fact afford multiarmed polymers.[5,6]

Recently a series of living radical polymerizations have been developed by us and others[4] where a dormant carbon−halogen terminal is reversibly activated (or transformed into a radical) via the redox reaction of transition-metal complexes including $RuCl_2(PPh_3)_3$,[7−13] $CuX(bpy)_n$ (X = Cl, Br),[14−20] $Ni\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}Br$,[21] $NiBr_2(PPh_3)_2$,[22] and $FeCl_2(PPh_3)_2$.[23] The terminal C−X bond is originated from an initiator with a similar C−X bond which undergoes homolytic cleavage by the metal compounds. The effective initiators for the Ru(II)-mediated living polymerization include not only carbon tetrachloride but also α-haloketones and α-haloesters.[8,12,13] As shown in eq 1, for example, with use of methyl dichloroacetate (**1a**), one of the C−Cl bonds is activated by the Ru(II) complex and changed into the C−Cl polymer terminal in the presence of aluminum compounds such as $Al(O\textit{i}Pr)_3$.[24] The aluminum com-

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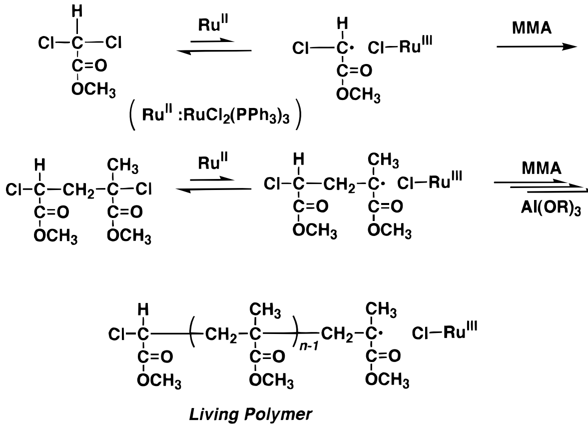
pounds are needed for faster living polymerizations with $RuCl_2(PPh_3)_3$.



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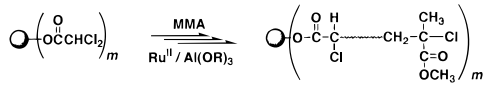
Following these leads, this study is to synthesize multiarmed polymers by the Ru(II)-catalyzed living radical polymerizations of MMA based on the multifunctional initiator method. The initiators employed herein possess two or three dichloroacetate units per molecule, where possible initiating points are linked through a spacer of alkyl (**2a** and **3a**) or aryl (**2b** and **3b**) esters (eq 2). The notations **2** and **3** denote bi- and trifunctional, respectively, whereas **a** and **b** mean an alkyl and an aryl spacer, respectively. They were then employed for living radical polymerization of MMA with $RuCl_2(PPh_3)_3$ in the presence of aluminum compounds. This paper will show that the use of $Al(acac)_3$ is crucial for the synthesis of multiarmed polymers with ester-type multifunctional initiators.



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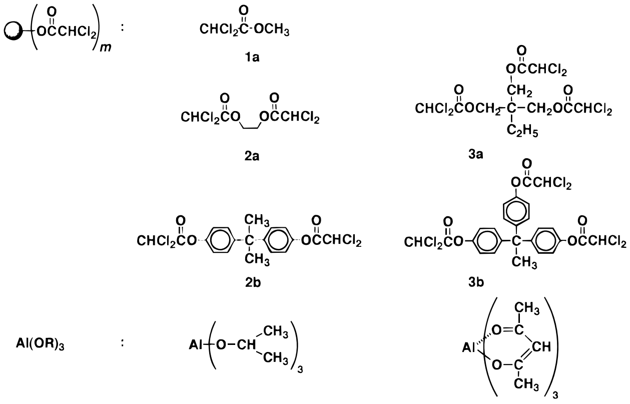

Results and Discussion

1. Synthesis of Multifunctional Initiators. The multifunctional initiators **2** and **3** were prepared by the reaction between dichloroacetyl chloride and a di- or trifunctional alcohol or phenol (eq 3; see also the Experimental Section). The products were purified by distillation or preparative size-exclusion chromatography.

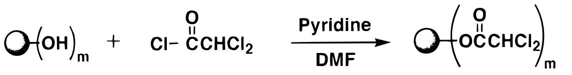

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Figure 1 shows the ^1H NMR spectra of the four initiators, all of which show the characteristic signal of the methine proton of dichloroacetate units around 6 ppm. In addition, there appeared the absorptions ascribed to their spacer units. The observed peak intensity ratios of the signals (shown in Figure 1) were in good agreement with the calculated values for the structures irrespective of the spacer units, confirming the formation of the di- and trifunctional dichloroacetates **2** and **3**.

2. Living Polymerization with Multifunctional Initiators. (a) Effects of Aluminum Compounds. The difunctional derivative initiator **2a** (with an ethylene glycol unit) was employed for the polymerization of MMA with $RuCl_2(PPh_3)_3$ in the presence of $Al(O\textit{i}Pr)_3$ in toluene at 80 °C ($[\mathbf{2a}]_0/[RuCl_2(PPh_3)_3]_0/[Al(O\textit{i}Pr)_3]_0 =$ 20/10/40 mM). The polymerization occurred smoothly and reached 90% in 50 h. Figure 2 shows the number-average molecular weights ($\overline{M}_n$) and the molecular weight distributions (MWDs) of the obtained polymers. The MWDs of the polymers were unimodal throughout the reaction. The $\overline{M}_n$ increased in direct proportion to monomer conversion but was lower than the calculated values assuming that one molecule of **2a** generates one living polymer chain (filled circles in Figure 2). The lower values turned out to be due to the transesterification between **2a** and $Al(O\textit{i}Pr)_3$, as described below. Noting this, we then employed $Al(acac)_3$ (acac: acetylacetonate), a Lewis acid considerably weaker than the isopropoxide, which might be reluctant to exchange an alkoxide unit with an ester. In contrast to the results with $Al(O\textit{i}Pr)_3$, the $\overline{M}_n$ values of the polymers obtained with $Al(acac)_3$ were in close agreement with the calculated values. The MWDs were also unimodal and relatively narrow.

The structures of the polymers were analyzed by ^1H NMR spectroscopy. Parts a and b of Figure 3 show the ^1H NMR spectra of the polymers obtained with initiator **2a** in the presence of $Al(acac)_3$ and $Al(O\textit{i}Pr)_3$, respectively. In Figure 3A, there can be seen a characteristic signal (*a*; 4.4 ppm) of the spacer ethylene glycol unit, in addition to the large absorptions of the main-chain repeat units (*c*−*e*), whereas the methine proton of the dichloroacetate unit in the initiator (6.0 ppm in Figure 1A) completely disappeared. Along with this, a new signal appeared at 4.3 ppm that is assigned to the methine proton (*b*) adjacent to one chlorine and one carbonyl group, as seen for 1-chloropropionates. This unit is generated via the conversion of one of the two C−Cl bonds in the dichloroacetate into the C−C bond via the addition of the carbon-centered radical to MMA [$Cl_2CHCO_2^- \rightarrow RClCHCO_2^-$; R = poly(MMA)]. The integrated peak intensity ratio of the initiator moiety ($a + b$) to the methyl ester protons (e) of the main chain [$6e/3(a + b)$] gives the number-average degree of the polymerizations ($\overline{DP}_n$) and, in turn, number-average molecular weights [$\overline{M}_n$(NMR)] based on ^1H NMR. The $\overline{M}_n$(NMR) is in good agreement with the $\overline{M}_n$ determined by size exclusion chromatography (SEC) [$\overline{M}_n$(NMR) = 8400; $\overline{M}_n$(SEC) = 8800]. The number-average arm numbers ($\overline{F}_n$) can thus be determined from $2\overline{M}_n(SEC)/\overline{M}_n(NMR)$. The obtained value, 2.10, is close to theoretical value, 2, which means that **2a** serves as a bifunctional initiator to give telechelic polymers in the presence of $Al(acac)_3$ and $RuCl_2(PPh_3)_3$.

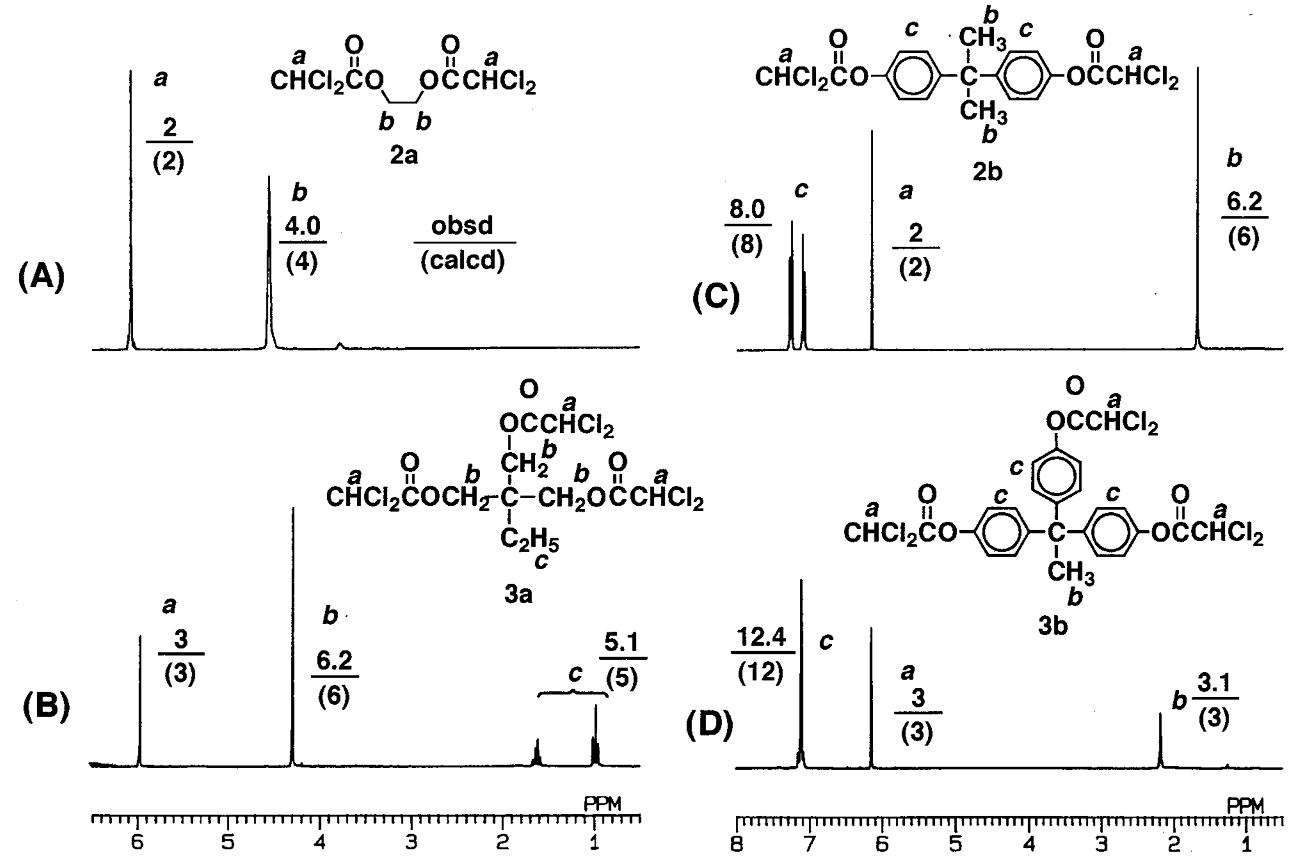


Figure 1. ^{1}H NMR spectra of multifunctional dichloroacetate initiators (see eq 2) in chloroform at 25 °C: (A) **2a**; (B) **3a**; (C) **2b**; (D) **3b**.

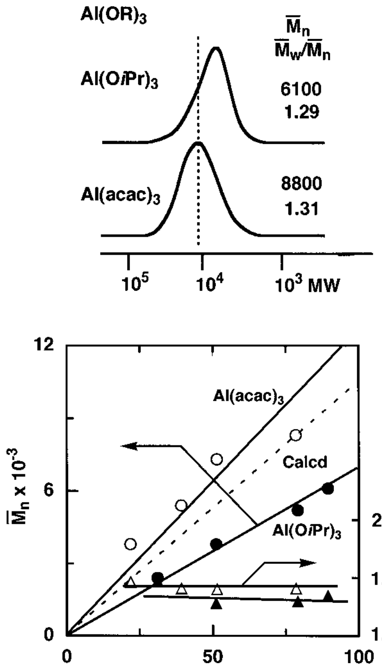
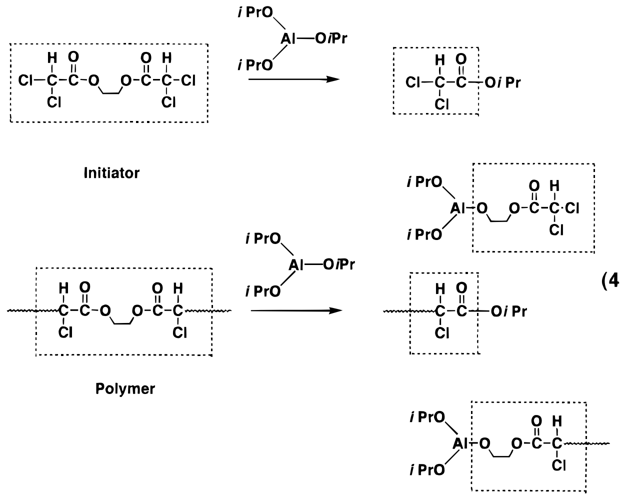


Figure 2. Effects of added aluminum compounds on the polymerization of MMA with **2a**/$RuCl_2(PPh_3)_3$ in toluene at 80 °C: $[M]_0$ = 2.0 M; $[\mathbf{2a}]_0$ = 20 mM; $[RuCl_2(PPh_3)_3]_0$ = 10 mM; $[Al(OR)_3]_0$ = 40 mM. Aluminum compound: (●, ▲) Al(O*i*Pr)$_3$; (○, △) Al(acac)$_3$.

According to our separate work,[8] the ω-ends of the polymers are most likely capped with a chlorine derived from the dichloroacetate, as also indicated by the small signal neighboring the main-chain peak (*e*).

In contrast, the polymers obtained with Al(O*i*Pr)$_3$ (Figure 3B) gave other absorptions (*f* and *f'*) in addition to the signals (*a*–*e*) observed in Figure 3A. The peak intensity of the spacer unit was smaller than that expected from the structure. Signal *f* is assigned to the methine proton of an isopropyl ester that is apparently generated via the transesterification between **2a** and Al(O*i*Pr)$_3$ (eq 4). This led to the decomposition of the



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ester linkage in **2a** and resulted in the formation of the corresponding monofunctional dichloroacetate, which should in turn act as an initiator. Thus, the chain length became about half that of the polymer chains obtained without such scission, and the molecular weights were lower than the calculated values, as shown

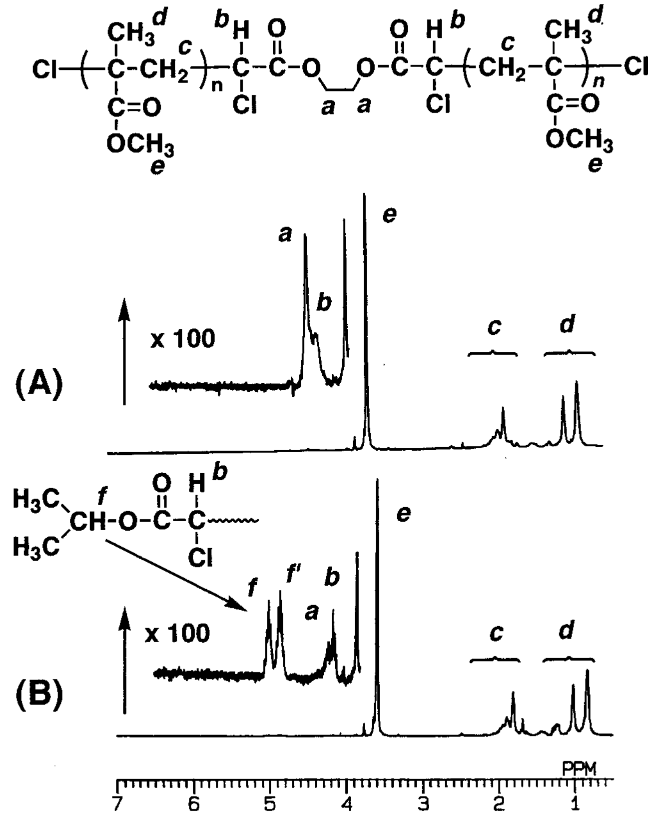

Figure 3. ^{1}H NMR spectra of poly(MMA) obtained with **2a**/RuCl$_2$(PPh$_3$)$_3$/Al(OR)$_3$ in toluene at 80 °C. Al(OR)$_3$: (A) Al(acac)$_3$ [$\overline{M}_n$(SEC) = 8800]; (B) Al(O*i*Pr)$_3$ [$\overline{M}_n$(SEC) = 4900].

in Figure 2. The other peak (*f'*) is assigned to the isopropyl ester proton generated by a similar transesterification reaction between the methyl ester in the main-chain PMMA units and Al(O*i*Pr)$_3$.[24] Such unfavorable reactions can be avoided with use of Al(acac)$_3$, probably due to the strongly coordinated acetylacetonate ligand. These results led us to employ Al(acac)$_3$ for the polymerization when coupled with ester-type multifunctional initiators.

(b) Polymerization with Alkyl Spacer-Type Initiators. A series of alkyl ester-type initiators (**1a**–**3a**) were then employed for the polymerizations of MMA in the presence of RuCl$_2$(PPh$_3$)$_3$ and Al(acac)$_3$ where the initiator concentrations were set at 20 mM ([initiator]$_0$/[RuCl$_2$(PPh$_3$)$_3$]$_0$/[Al(acac)$_3$]$_0$ = 20/10/8.0 mM). Thus, the concentrations of the dichloroacetate units were 20 mM for **1a**, 40 mM for **2a**, and 60 mM for **3a**. Irrespective of the number of the dichloroacetate units, the $\overline{M}_n$ increased in direct proportion to monomer conversion (Figure 4). The $\overline{M}_n$ slightly depended on the initiator functionality but invariably agreed closely with the calculated values. The broad MWD with **1a** is probably due to the relatively slow initiation from the C–Cl bond.[13] The MWDs became narrower with the increase in the number of arms. This is ascribed to the averaging of the difference in chain lengths by the increase of the number of arms per polymer molecule. These results show that all these multifunctional initiators with alkyl spacers induce living radical polymerizations of MMA when coupled with RuCl$_2$(PPh$_3$)$_3$ and Al(acac)$_3$.

To further demonstrate the multifunctionality of the initiation, the polymerization with use of 6.7 mM of **3a** was carried out in conjunction with RuCl$_2$(PPh$_3$)$_3$ and Al(acac)$_3$, where the concentration of the dichloroacetate units was equal to 20 mM, the same as for the monofunctional version **1a**. As shown in Figure 5, the $\overline{M}_n$ increased in direct proportion to monomer conversion, and the MWDs were narrow throughout the reaction. The $\overline{M}_n$ values with **3a** were three times higher than those with the same mole concentration of the monofunctional initiator **1a**. These results indicate that all three dichloroacetate functions in **3b** indeed initiate

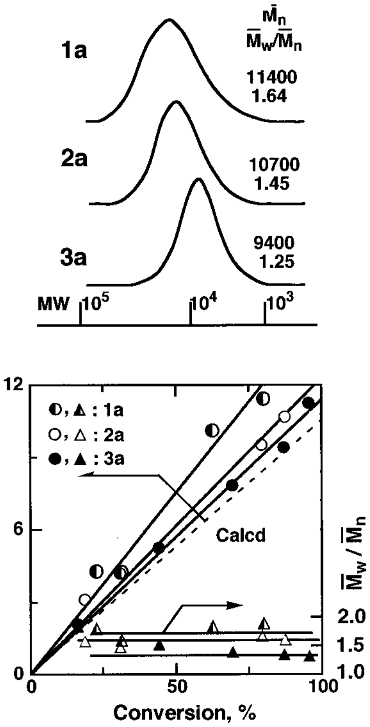

Figure 4. Polymerizations of MMA with alkyl-spacer type initiators (**1a**, **2a**, and **3a**) in conjunction with RuCl$_2$(PPh$_3$)$_3$ and Al(acac)$_3$ in toluene at 80 °C. [M]$_0$ = 2.0 M; [initiator]$_0$ = 20 mM; [RuCl$_2$(PPh$_3$)$_3$]$_0$ = 10 mM; [Al(acac)$_3$]$_0$ = 8.0 mM.

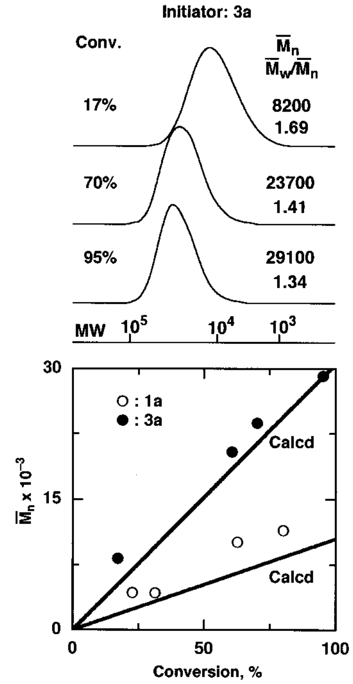

Figure 5. Polymerizations of MMA with **3a**/RuCl$_2$(PPh$_3$)$_3$/Al(acac)$_3$ in toluene at 80 °C. [M]$_0$ = 2.0 M; [**3a**]$_0$ = 6.7 mM; [RuCl$_2$(PPh$_3$)$_3$]$_0$ = 10 mM; [Al(acac)$_3$]$_0$ = 8.0 mM.

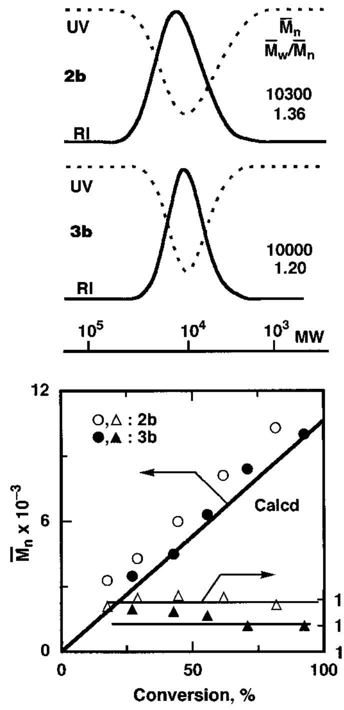

Figure 6. Polymerizations of MMA with aryl spacer-type initiators (**2b** and **3b**) in conjunction with $RuCl_2(PPh_3)_3$ and $Al(acac)_3$ in toluene at 80 °C. $[M]_0 = 2.0$ M; $[\text{initiator}]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(acac)_3]_0 = 8.0$ mM.

living polymerization of MMA without being scissored by side reactions such as transesterification. Separate experiments also show that only one of the two geminal chlorines next to the ester carbonyl in **1a**–**3a** initiates radical polymerization.

(c) Polymerization with Aryl Spacer-Type Initiators. Polymerization of MMA was also carried out with the use of the aryl ester type-initiators (**2b** and **3b**). These initiators also induced quantitative polymerization of MMA in the presence of $RuCl_2(PPh_3)_3$ and $Al(acac)_3$ in toluene at 80 °C. As shown in Figure 6, the $\overline{M}_n$ was directly proportional to monomer conversion and in agreement with the calculated values. The MWDs were unimodal and became narrower with increase of the number of the acetate units. The aryl spacer-type initiators gave narrower MWDs than the alkyl counterparts did, and the polymers obtained with **2b** and **3b** showed ultraviolet absorption in SEC analysis. The ultraviolet (dashed lines) and the refractive-index (solid lines) traces were almost identical over the entire molecular weight range. These absorptions thus demonstrate the inclusion of the aromatic initiator residues into the polymer chains. The aryl spacer-type initiators are thus effective for the Ru(II)-mediated living polymerization of MMA in the presence of $Al(acac)_3$.

The polymer structures obtained with **3b** were then analyzed by ^1H NMR (Figure 7). The spectrum gives the absorption (*b*) of the aromatic groups of the spacer of **3b**, in addition to that of the main-chain repeat units (*d*–*f*). The methine proton at 6.2 ppm, assigned to the dichloroacetate units (see Figure 2D), completely disappeared and in turn gave a new signal (*a*) at 4.3 ppm due to the monochloroacetate methine $RClCHCO_2^-$ (cf. Figure 3A). These indicate that **3b** initiates living polymerizations of MMA and results in three-armed polymers.

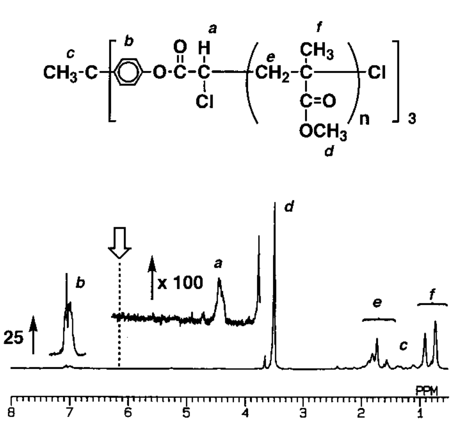

Figure 7. ^1H NMR spectrum of poly(MMA) obtained with **3b**/$RuCl_2(PPh_3)_3$/$Al(acac)_3$ in toluene at 80 °C: $\overline{M}_n(\text{NMR}) = 8200$; see also Table 1. The double arrow indicates the signal position for $CCl_2CHCO_2^-$ that the unreacted initiation sites of **3b** would exhibit.

Table 1. $\overline{M}_n$, $\overline{M}_w/\overline{M}_n$, and $\overline{F}_n$ of Poly(MMA) Obtained with Initiator/$RuCl_2(PPh_3)_3$/$Al(acac)_3$[a]

initiator[b]	$\overline{M}_n$(SEC)	$\overline{M}_n$(NMR)[c]	$\overline{M}_w/\overline{M}_n$	$\overline{F}_n$[d]
1a	4900	4900	1.40	1.00
2a	4500	4900	1.30	1.84
	11000	11600	1.38	1.90
2b	7000	6500	1.37	2.14
	9400	10000	1.37	1.90
3a	8500	9200	1.30	2.79
	10200	10500	1.25	2.91
3b	9000	8200	1.20	3.27
	11400	10300	1.20	3.31

[a] $[M]_0/[\text{initiator}]_0/[RuCl_2(PPh_3)_3]_0/[Al(acac)_3]_0 = 2000/20/10/8.0$ mM; in toluene, at 80 °C. [b] See eq 2 for structures **1a**–**3b**. [c] From ^1H NMR peak intensity ratio: see Figures 3 and 7, for example. [d] $\overline{M}_n(\text{SEC})/\overline{M}_n(\text{NMR})$.

As discussed already, the integration of the peak intensity ratios gave $\overline{M}_n$(NMR) and number-average arm-numbers ($\overline{F}_n$). Table 1 summarizes the results for the polymers obtained with the four multifunctional initiators (**2** and **3**) and their monofunctional analogue **1a**. The $\overline{F}_n$ values are invariably close to the initiators functionality. As for the triesters, however, there is some difference in $\overline{F}_n$ between the alkyl- and aryl-type initiators. Although the $\overline{F}_n$ lower than 3 with **3a** may suggest incomplete initiation, there can be seen no residual peaks of the dichloroacetate units at 6 ppm in the spectra of the polymers from **3b** (see Figure 7). These may relate to the branching structure of the polymers that affect the $\overline{M}_n$(SEC).

In conclusion, the esters **2** and **3** with two and three dichloroacetate units initiate living radical polymerization of MMA catalyzed by $RuCl_2(PPh_3)_3$ in the presence of $Al(acac)_3$ to give telechelic and triarmed polymers, respectively. With these ester-type multifunctional initiators, the use of $Al(acac)_3$ is crucial for the synthesis of the multiarmed polymers to be free from the transesterification between the ester group in the initiator units and the added aluminum alkoxides.

Experimental Section

Synthesis of Multifunctional Initiators. Difunctional ester **2a** was prepared by the reaction between dichloroacetyl chloride and ethylene glycol. In a 500-mL round-bottomed flask filled with dry nitrogen, dichloroacetyl chloride (45.0 mL; 0.468 mol) was added dropwise to a solution of ethylene glycol

(11.7 mL; 0.210 mol) and pyridine (45.5 mL; 0.563 mol) in dimethylformamide (75 mL). The reaction mixture was stirred at room temperature for 24 h and poured into 300 mL of water. The aqueous phase was extracted with four 300-mL portions of diethyl ether, and the ether extracts were combined with the organic layer. The combined organic phase was washed with water (300 mL) and dried with sodium sulfate overnight. After the ether was removed by evaporation, the crude products were distilled under reduced pressure to give **2a** (bp 135 °C/0.5 Torr); purity > 98% by ^{1}H NMR (Figure 1A).

The other three functionalized initiators (**2b**, **3a**, and **3b**) were also prepared by similar methods; **2b** and **3a** were purified by preparative size-exclusion chromatography (SEC) (column, Shodex H-2001; exclusion limit = 1×10^3; 2.5-cm i.d. × 50 cm) in chloroform; **3b** was purified by column chromatography (Silica Gel 60; 4.0 cm i.d. × 40 cm) in methylene chloride. The purity of all these compounds was confirmed by ^{1}H NMR (purity > 98%; Figure 1B−D).

Other Materials. MMA (Tokyo Kasei; purity > 99%) was dried overnight over calcium chloride and distilled twice over calcium hydride under reduced pressure before use. Methyl dichloroacetate (**1a**; Tokyo Kasei; purity > 99%) was dried overnight over calcium chloride and doubly distilled over calcium hydride under reduced pressure before use. $RuCl_2(PPh_3)_3$ (Merck; purity > 99%), $Al(O\textit{i}Pr)_3$ (Aldrich; purity > 99.99%), and $Al(acac)_3$ (Aldrich; purity > 99%) were used as received. Toluene (solvent) and *n*-octane (internal standard for gas chromatography) were dried overnight over calcium chloride, distilled twice over calcium hydride, and bubbled with dry nitrogen for more than 15 min immediately before use.

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 tubes. A typical example is given below. The polymerization was initiated by adding solutions of $Al(acac)_3$ (0.02 mmol in 0.80 mL) and $RuCl_2(PPh_3)_3$ (0.025 mmol in 1.0 mL) in toluene, sequentially in this order, into a mixture (0.70 mL) of MMA (0.54 mL; 5.0 mmol), *n*-octane (0.16 mL), and **2a** (0.05 mmol) in toluene at room temperature. The total volume of the reaction mixture was thus 2.5 mL. Immediately after mixing, the solution was placed in a water bath kept at 80 °C. 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 a solid, porous absorbent [Kyowaad-2000G-7 ($Mg_{0.7}Al_{0.3}O_{1.15}$); Kyowa Chemical] (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.

Measurements. The MWD, $\overline{M}_n$, and $\overline{M}_w/\overline{M}_n$ ratios of the polymers were measured by SEC in chloroform at 40 °C on three linear-type polystyrene gel columns (Shodex K-805L; exclusion limit = 5×10^6; 0.8 cm i.d. × 30 cm) that were connected to a Jasco PU-980 precision pump, a Jasco RI-930 refractive index detector, and a Jasco UV-970 UV/vis detector set at 256 nm. The columns were calibrated against 11 standard poly(MMA) samples (Polymer Laboratories; $\overline{M}_n$ = 630−220000; $\overline{M}_w/\overline{M}_n = 1.06-1.22$) as well as the monomer. ^{1}H NMR spectra were recorded in $CDCl_3$ at 25 °C on a JEOL JNM-GSX270 spectrometer, operating at 270.7 MHz. Polymers for ^{1}H NMR analysis and reinitiation were fractionated by preparative SEC (column, Shodex K-2002; exclusion limit = 5×10^3; 2.0 cm i.d. × 30 cm).

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