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Calixarene-Core Multifunctional Initiators for the Ruthenium-Mediated Living Radical Polymerization of Methacrylates[1]

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ABSTRACT: Tetra-, hexa-, and octafunctional initiators constructed with calix[*n*]arene cores ($n = 4$, 6, and 8) and dichloroacetate units led to living radical polymerization of methyl methacrylate (MMA) to give star polymers with four, six, and eight arm chains of controlled lengths, respectively, when coupled with $RuCl_2(PPh_3)_3$ and $Al(OiPr)_3$ in toluene at 80 °C. The produced polymers had controlled molecular weights and narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n = 1.1-1.2$). Hydrolysis of the ester linkage between the core and the arm chains gave linear polymers whose number-average molecular weights are almost $^1/_4$, $^1/_6$, and $^1/_8$ of those for tetra-, hexa-, and octaarmed star polymers, respectively, consistent with the arm numbers expected from the initiator functionality. Octaarmed star polymers consisting of block copolymers of MMA and *n*-butyl methacrylate as arm chains were also synthesized by the sequential block copolymerizations initiated with the calix[8]arene-based initiator in conjunction with $RuCl_2(PPh_3)_3$ and $Al(OiPr)_3$.

Introduction

A star polymer is defined as a polymer that consists of multiple linear chains linked together at one end of each chain by a junction point.[2] Star polymers are of interest because of their unique spatial shapes and lower viscosity compared with that of linear polymers with similar molecular weights. Regular star polymers have a single branch point and all arms exhibit low degrees of compositional heterogeneity with respect to molecular weight and molecular weight distributions (MWDs).[2d] Living polymerizations are ideally suited for the preparation of such star polymers with well-defined structures.

Star polymers obtained by living polymerizations can be categorized roughly into two types from the viewpoint of degree of structural uniformity: (1) star polymers with nearly uniform arm lengths but with statistical distribution in the number of arms per molecule and (2) star polymers with nearly uniform arm lengths and with a predetermined number of arms. The former type are synthesized by (i) living polymerizations from microgels prepared from a divinyl compound or (ii) linking reaction of linear living polymers with a divinyl compound, whereas the latter are synthesized by (iii) living polymerization from a multifunctional initiator with a defined number of initiating function or (iv) coupling reaction of linear living polymers with a multifunctional quencher with a defined number of quenching function. In general, star polymers obtained by methods i and ii have relatively large numbers of arms ($\sim 10-10^3$), in contrast to small numbers (3−8) based on methods iii and iv, but the latter methods give products of well-defined and predetermined arm numbers.

For example, star polymers have been extensively prepared by anionic living polymerizations via method i or ii, where they consist of less polar arm polymers such as polystyrene and polydienes, etc., and cores mostly derived from divinylbenzene.[2a−e] Star polymers with a precise number of arms were obtained by method iv with multifunctional quenchers such as silyl halides for lithium anions of living polymers. The multifunctional initiator method, iii, is generally less frequently employed in anionic living polymerizations because of the low solubility of multifunctional organolithium initiators in hydrocarbon solvents. In contrast, effective multifunctional initiators for living cationic polymerizations are available, which are metal-free compounds with multiple halide, acetate, or ether groups as multifunctional initiating points.[2f,g] Metal-free silicon-based group-transfer polymerizations permit the synthesis of three- or four-arm star poly(methyl methacrylate)s (PMMAs) with use of soluble multifunctional initiators,[3,4] and star PMMAs with higher number ($\sim$10−100) of arms were prepared by linking reaction method with use of divinyl methacrylates.[5,6]

In contrast to such a variety of star polymers that have been prepared by anionic and cationic living polymerizations, similar synthesis by radical polymerizations has been difficult due to substantial lack of living or controlled polymerizations. However, recent progresses in living radical polymerizations have permitted the control of molecular weights and MWDs nearly comparable to those prepared by ionic living polymerizations.[7] These living or controlled systems can be achieved, in general, either by the capping of the polymer terminal with a stable nitroxide radical[8,9] or by the activation (radical cleavage) of a stable carbon−halogen bond with a transition metal complex (eq 1).[10,11] These controlled radical polymerizations have been applied for the synthesis of well-controlled block and end-functionalized polymers. Recently, for example, we have synthesized telechelic and triarmed PMMAs of controlled molecular weights and MWDs for ruthenium-catalyzed living radical polymerizations with use of di- and trifunctional initiators, respectively.[12] Nitroxide-mediated living radical polymerizations enabled the synthesis of triarmed polystyrene with use of a trifunctional initiator.[13]

This study is to prepare regular star polymers of PMMA with a higher number of arms (>3) by the Ru(II)-catalyzed living radical polymerizations initiated by well-defined multifunctional initiators. For this, we

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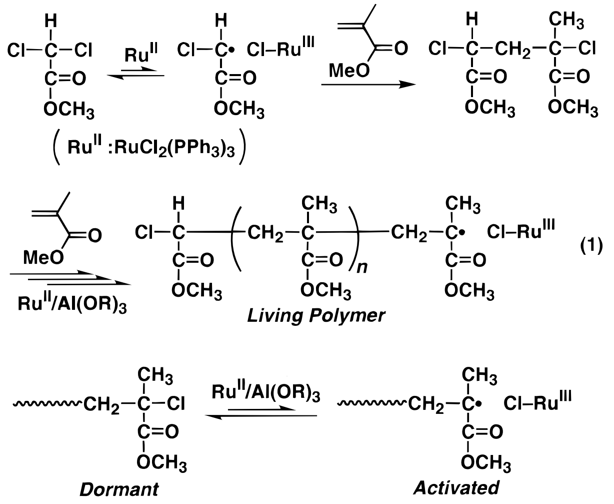

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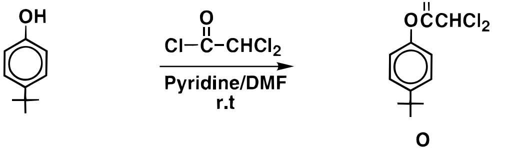
employed a series of calix[*n*]arenes ($n = 4$, 6, and 8) as core parts of the multifunctional initiators with several dichloroacetate units attached thereto as initiating points (Scheme 1). Calixarenes are a class of phenol-containing macrocycles that can be prepared by condensation of para-substituted phenol and formaldehyde, and their ring sizes can be precisely controlled by synthetic conditions.[14] These compounds are of interest as hosts for small organic molecules by hydrophobic interaction with the condensed aromatic groups. The use of calixarenes as core units may afford not only the precise control of the number of functional groups but also special function due to the spatial shape of calixarene.[14] Recently, Kennedy and co-workers prepared an octafunctional initiator from calix[8]arene and further obtained eight armed polyisobutylene by living cationic polymerization of isobutylene.[15] Independently we have been pursuing the use of these calixarene-based multifunctional initiators for living radical polymerizations.[1] In this paper, we show that calix[*n*]arene-core multifunctional initiators ($n = 4$, 6, 8) induce living polymerizations of MMA in the presence of $RuCl_2(PPh_3)_3$ and $Al(OiPr)_3$ to generate regular star PMMAs with four, six, and eight arms.

Results and Discussion

1. Synthesis of Calixarene-Core Multifunctional Initiators. Hexa- and octafunctional initiators, **3** and **4**, were prepared by the reactions between dichloroacetyl chloride and calix[6]- and calix[8]arenes, respectively; a monofunctional counterpart **1** was also obtained similarly (eqs 2 and 3). A tetrafunctional initiator, **2**, cannot be obtained by such a direct reaction of the acid chloride with calix[4]arene but with its lithium salt (eq 4). The difficulty in the direct reaction is probably due to the strong hydrogen bonding of the phenolic groups in such a small calixarene. These products were purified by recrystallization from $CHCl_3$/methanol (see also the Experimental Section).



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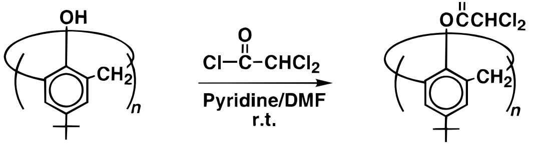

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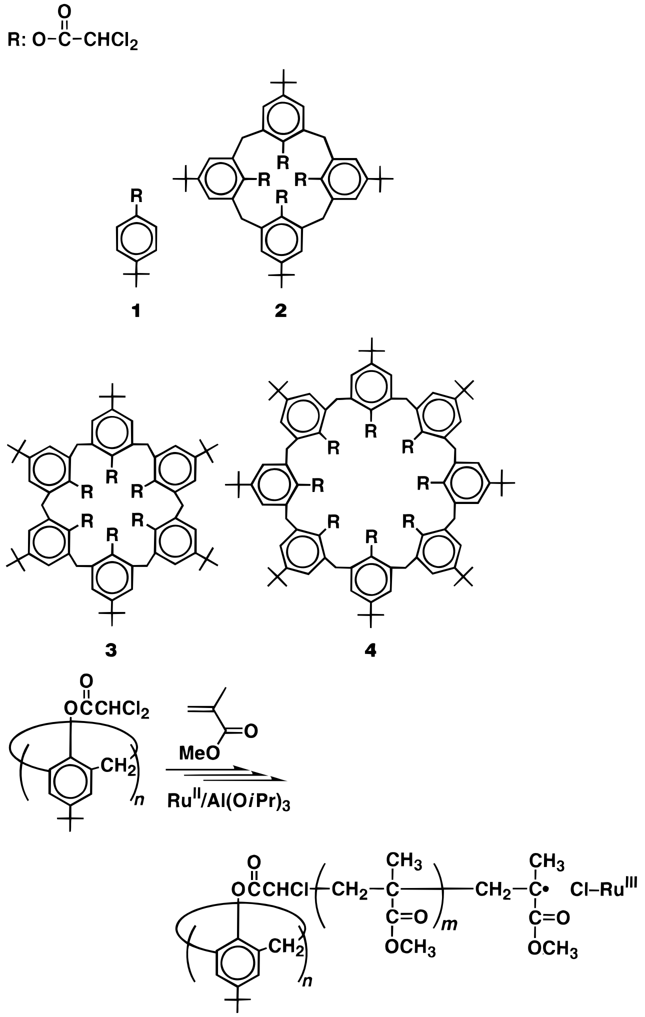
3 ($n = 6$), **4** ($n = 8$)

Scheme 1



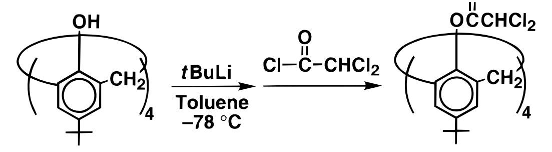


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Figure 1 shows the ^1H NMR spectra of the four multifunctional initiators, all of which show the characteristic signals of the methine proton (*d*) of dichloroacetate units around 6 ppm. Also observed were the absorptions of the aromatic and *tert*-butyl groups around 7 and 1 ppm, respectively, which are due to the calixarene cores. The signals of the calix[4]arene-type initiator are complicated because of several conformations that are difficult to interconvert from one to another because of its rigid small ring structure. In contrast, the calix[6]- and calix[8]arene-based initiators gave single and broad absorptions, where broadening of the signals is due to slow interconversion of several conformations. The observed peak intensity ratios

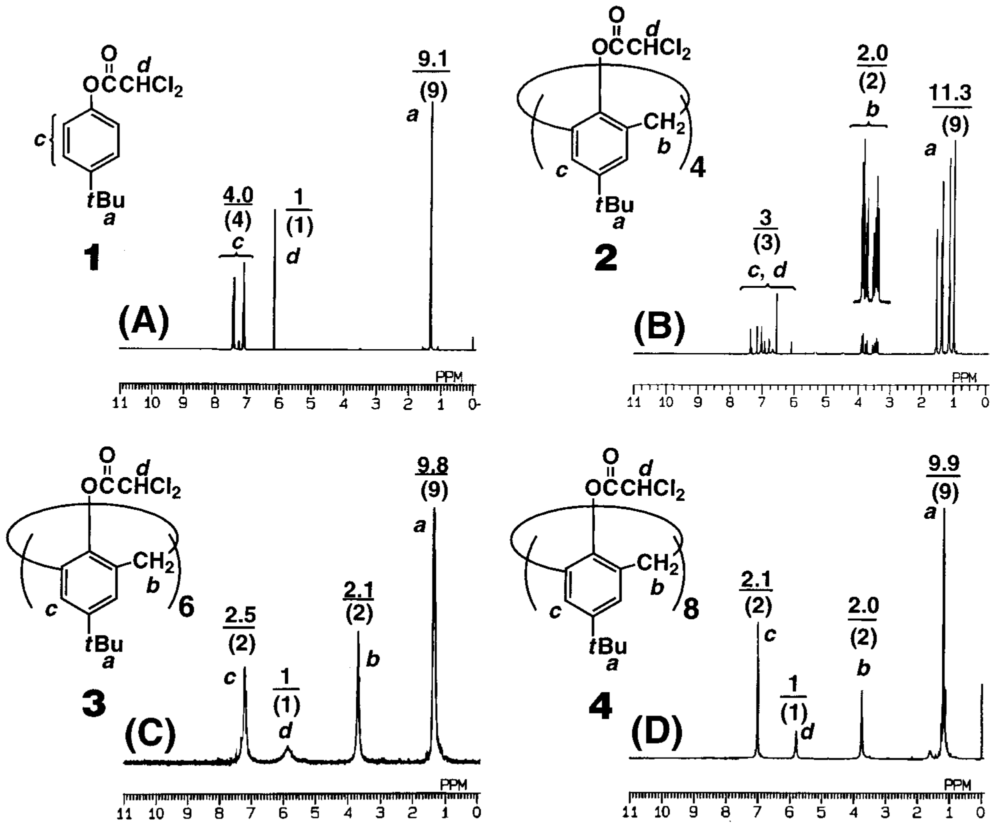


Figure 1. ^{1}H NMR spectra of multifunctional dichloroacetate initiators in $CDCl_3$ at 25 °C: (A) **1**; (B) **2**; (C) **3**; (D) **4** (see also Scheme 1 for structures).

(shown in Figure 1) were in good agreement with the calculated values for the expected structures irrespective of the core units, confirming the formation of the mono-, tetra-, hexa-, and octafunctional initiators of dichloroacetate, **1**, **2**, **3**, and **4**, respectively.

2. Living Polymerization with Multifunctional Initiators. The monofunctional initiator **1** (with a *p-tert*-butylphenol unit) was first 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 ($[\mathbf{1}]_0/[RuCl_2(PPh_3)_3]_0/[Al(O\textit{i}Pr)_3]_0 = 20/10/40$ mM). The polymerization occurred smoothly and reached 90% in 50 h. Figure 2 shows the number-average molecular weights ($\bar{M}_n$) and the molecular weight distributions (MWDs) of the obtained polymers. The MWDs of the polymers were unimodal throughout the reaction. The $\bar{M}_n$ increased in direct proportion to monomer conversion. However, the ^{1}H NMR spectrum of the polymers obtained with **1** in the presence of $Al(O\textit{i}Pr)_3$ shows that the transesterification between **1** and $Al(O\textit{i}Pr)_3$ occurred, as will be discussed below.

A series of calixarene-core initiators (**2**−**4**) were then employed for the polymerizations of MMA in the presence of $RuCl_2(PPh_3)_3$ and $Al(O\textit{i}Pr)_3$ where the concentration of the dichloroacetate units were set constant at 20 mM ($[CHCl_2CO_2-]_0/[RuCl_2(PPh_3)_3]_0/[Al(O\textit{i}Pr)_3]_0 = 20/10/40$ mM). Thus, the concentrations of the initiators were 5.0 mM for **2**, 3.3 mM for **3**, and 2.5 mM for **4**. Irrespective of the number of the dichloroacetate units, the $\bar{M}_n$ increased in direct proportion to monomer conversion (Figure 3). The molecular weight distributions were narrow throughout the reaction ($\bar{M}_w/\bar{M}_n = 1.1-1.2$) irrespective of the initiators, as shown in the size-exclusion chromatograms (SEC traces) for the polymers obtained with **4**. They showed ultraviolet absorptions, and the UV traces are almost identical to the refractive index traces over the entire molecular weight range. The UV absorption demonstrates the incorporation of the calixarene unit into the polymers independent of their molecular weights.

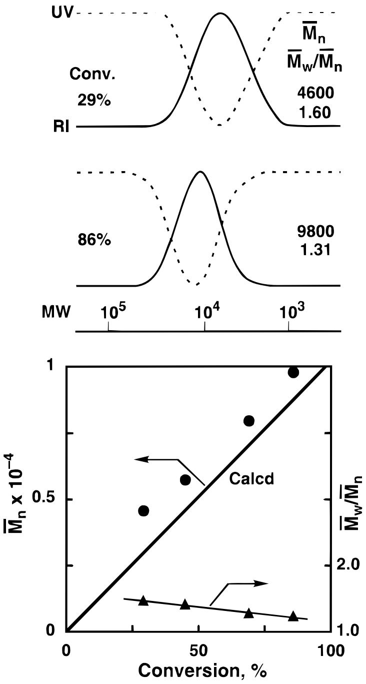


Figure 2. Polymerization of MMA with monofunctional initiator (**1**) in conjunction with $RuCl_2(PPh_3)_3$ and $Al(O\textit{i}Pr)_3$ in toluene at 80 °C. $[M]_0 = 2.0$ M; $[\mathbf{1}]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(O\textit{i}Pr)_3]_0 = 40$ mM.

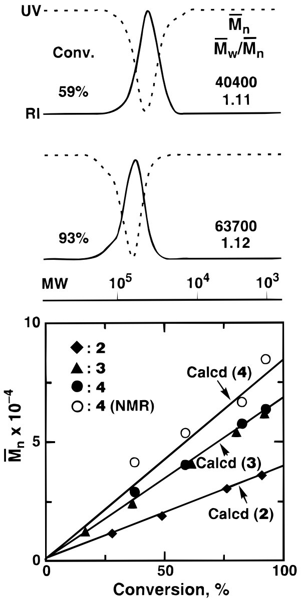


Figure 3. Polymerization of MMA with multifunctional initiators (**2**, **3**, and **4**) in conjunction with $RuCl_2(PPh_3)_3$ and $Al(O\textit{i}Pr)_3$ in toluene at 80 °C. $[M]_0 = 2.0$ M; $[\mathbf{2}]_0 = 5.0$ mM (◆); $[\mathbf{3}]_0 = 3.3$ mM (▲); $[\mathbf{4}]_0 = 2.5$ mM (●, ○); $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(O\textit{i}Pr)_3]_0 = 40$ mM.

The $\bar{M}_n$ clearly depended on the initiator functionality, and especially with **2** and **3**, they agreed well with calculated values assuming that one molecule of the initiator generates one molecule of polymers consistent with their functionality. However, with the octafunctional initiator, **4**, the $\bar{M}_n$ values based on SEC (filled circles) were slightly lower than the calculated values. In contrast, the $\bar{M}_n$ values based on ^{1}H NMR spectroscopy (open circles; see below) were in good agreement with calculated values and directly proportional to monomer conversion. The lower molecular weights measured by SEC are most probably due to the difference in exclusion volume between star-shaped and linear polymers.

The structures of the polymers were then analyzed by ^{1}H NMR spectroscopy. Figure 4, parts A and B, show the ^{1}H NMR spectra of the polymers obtained with **1** and **4**, respectively. In Figure 4A, there can be seen the large absorptions of the main-chain repeat units (*a*–*c*), 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 which is assigned to the methine proton (*d*) 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 = PMMA]. In addition to these signals, there can be seen a signal (*e*′) which is assigned to the methine proton of an isopropyl ester that is apparently generated via the transesterification between **1** and $Al(O\textit{i}Pr)_3$. Also, the spectrum exhibited similar isopropyl ester groups (*e*) generated via exchange reactions between the methyl ester in PMMA units and $Al(O\textit{i}Pr)_3$, where, however, the amount of such isopropyl ester units in main chain is very low relative to the intact methyl esters in PMMA.

In contrast, the polymers obtained with calix[8]arene core initiator, **4**, did not show the absorption of the methine proton (*e*′) attributed to the terminal isopropyl ester generated from the transesterification, or the absence of decomposition of ester linkage in **4**, which warrants the formation of eight-armed polymers. The same conclusion was reached for the other calixarene-core initiators, **2** and **3**. This is due to the bulky and crowded environment around the calix core moiety that prevents such transesterification with $Al(O\textit{i}Pr)_3$. However, neither the signals of the methine proton (*d*) adjacent to one chlorine and one carbonyl group nor of the aromatic protons of the calixarene cores was seen probably due to the low mobility of the core part.

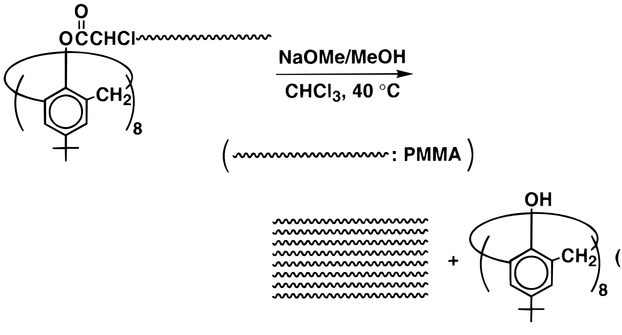
Table 1. $\bar{M}_n$ **and** $\bar{F}_n$ **of Star PMMA Obtained with Multifunctional Initiators/**$RuCl_2(PPh_3)_3/Al(O\textit{i}Pr)_3$ **and** $\bar{M}_n$ **of Arm PMMA after Scission**[a]

initiator[b]	star PMMA: $\bar{M}_n$(SEC)	star PMMA: $\bar{M}_n$(NMR)[c]	arm PMMA: M_n(SEC)	$\bar{F}_n$[d]
2	19900	22500	6000	3.75
	32000	32700	9200	3.55
3	11800	12500	2200	5.68
	20800	21300	3800	5.61
4	60300	66700	8000	8.34
	66100	73100	8800	8.34

[a] $[M]_0/[CHCl_2CO_2-]_0/[RuCl_2(PPh_3)_3]_0/[Al(O\textit{i}Pr)_3]_0 = 2000/20/10/40$ mM; in toluene, at 80 °C. [b] See Scheme 1 for structures **2**–**4**. [c] $\bar{M}_n$(NMR) = $(c/c') \times f$ (f = number of dichloroacetate units in initiators): see Figure 4, for example. [d] $\bar{M}_n$(star PMMA, NMR)/$\bar{M}_n$(arm PMMA, SEC).

The number-average degree of the polymerizations ($\bar{DP}_n$) and, in turn, number-average molecular weights [$\bar{M}_n$(NMR)] based on ^{1}H NMR, can be obtained from the methyl ester protons (*c*) of the main chain and the ω-end's methyl ester protons (*c*′) of the polymers. Table 1 summarizes the molecular weights for these star polymers obtained by SEC and NMR. The NMR-based values were in good agreement with those by SEC for the polymers obtained with tetra- (**2**) and hexafunctional (**3**) initiators. As mentioned above, for the polymers with **4** the values by NMR were larger than those on SEC and in good agreement with the calculated values.

3. Arm Scission of the Star Polymers. The arm polymers obtained with the calixarene-core initiators should be connected to the cores via ester linkages that can be hydrolyzed into calixarene core and chain arms (eq 5). To confirm the number of these arm chains, hydrolysis of the ester linkages was carried out with sodium methoxide in a mixed solvents of methanol and chloroform at 40 °C. Figure 5 shows the SEC eluograms of the polymers obtained after hydrolysis, along with the precursor star polymers and the initiators. After the hydrolysis, the main SEC peaks moved to lower molecular weights along with the generation of new sharp peaks around peak molecular weight of 1000 with



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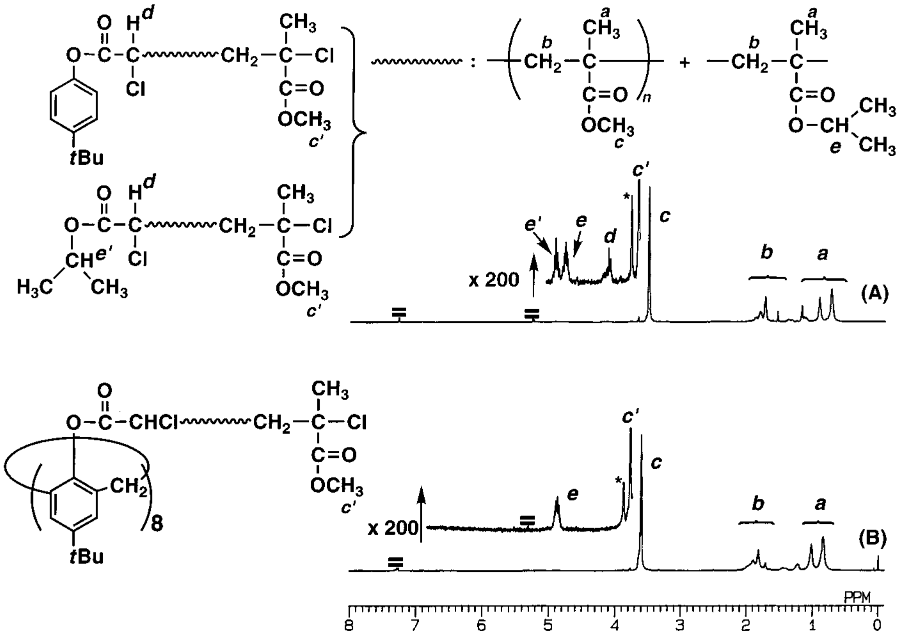

Figure 4. ^{1}H NMR spectra of poly(MMA) obtained with initiators (**1** and **4**) in conjunction with $RuCl_2(PPh_3)_3/Al(O\textit{i}Pr)_3$ in toluene at 80 °C: (A) **1** [$\bar{M}_n$(SEC) = 6700]; (B) **4** [$\bar{M}_n$(SEC) = 60 300, $\bar{M}_n$(NMR) = 66 700]. The signals marked by an asterisk are ^{13}C satellite lines.

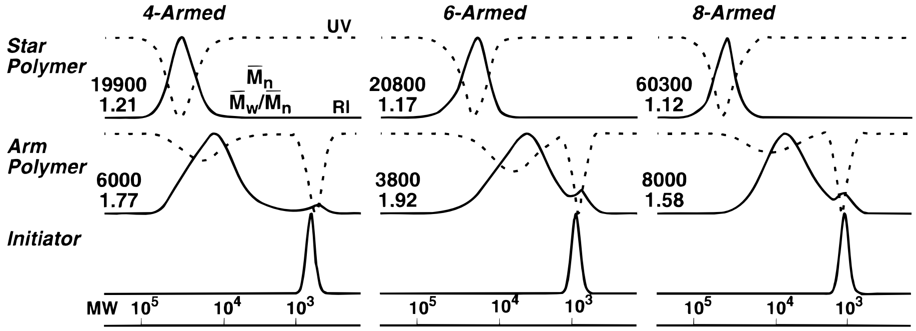

Figure 5. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of star poly(MMA), and products after scission of the star poly(MMA), and initiators **2**, **3**, and **4**.

strong UV absorptions whose molecular weights were almost the same with the calixarene cores. The $\bar{M}_n$ after scission were almost $^1/_4$, $^1/_6$, and $^1/_8$ of those for star polymers, respectively (Table 1). Thus, we can calculate the average number of arms ($\bar{F}_n$) from the ratio of $\bar{M}_n$(NMR) of star polymers to $\bar{M}_n$(SEC) of the arm polymers. The $\bar{F}_n$ were nearly equal to the numbers of the dichloroacetate units in the initiators, and it showed that the calix[4]-, [6]-, and [8]arene-based units really act as multifunctional initiators to give star polymers with tetra-, hexa- and octaarms, respectively. However, the MWDs of the arm polymers were broader than those for the star polymers due to differences in arm lengths, which are masked in star polymers schematically obtained by connecting the arms together into the cores. Similar results were obtained with star-shaped poly(isobutylene) prepared by calixarene-based initiators.[15] This suggests that there are some differences in arm chain length due to slow initiation from the dichloroacetate initiating points or slow interconversion between dormant and activated species.

4. Star-Shaped Block Copolymers. Block copolymerization of MMA and *n*-butyl methacrylate (BMA) was examined with a calixarene-core initiator in the presence of $RuCl_2(PPh_3)_3$ and $Al(O\textit{i}Pr)_3$. For this, MMA was first polymerized with the octafunctional initiator, **4**, coupled with $RuCl_2(PPh_3)_3$ and $Al(O\textit{i}Pr)_3$ in toluene at 80 °C. After the nearly complete consumption of MMA, a fresh feed of BMA, 2 mol equiv to MMA, was added into the living star PMMA thus obtained [$\bar{M}_n$(SEC) = 27 100, $\bar{M}_w/\bar{M}_n$ = 1.14]. The second monomer was smoothly polymerized, and as shown in Figure 6, the MWD shifted to higher molecular weight while keeping a narrow MWD [$\bar{M}_n$(SEC) = 85 200, $\bar{M}_w/\bar{M}_n$ = 1.10].

Figure 7 shows ^{1}H NMR spectra of the PMMA (A; the starting living chains) and the block copolymers with BMA (B) obtained therefrom with **4** in the presence of $RuCl_2(PPh_3)_3/Al(O\textit{i}Pr)_3$. In Figure 7B, the signals of the BMA repeat units are seen, in addition to the MMA units. The unit ratio of MMA to BMA was obtained from the peak intensity ratio of the ester methyl protons (*c*) in the MMA unit to the ester methylene protons (*d*) in the BMA unit. The observed ratio, 1.95 (BMA/MMA), was in good agreement with the calculated value (1.90) from the monomer feed ratio and the gas chromatographic conversions. Furthermore, the absence of the terminal methyl ester protons (*c*′), adjacent to the chlorine atom at the *ω*-end, indicates nearly quantitative blocking of BMA from the living PMMA terminal to produce AB-block eight-armed star polymers. Similar star-shaped block copolymers were also obtained by

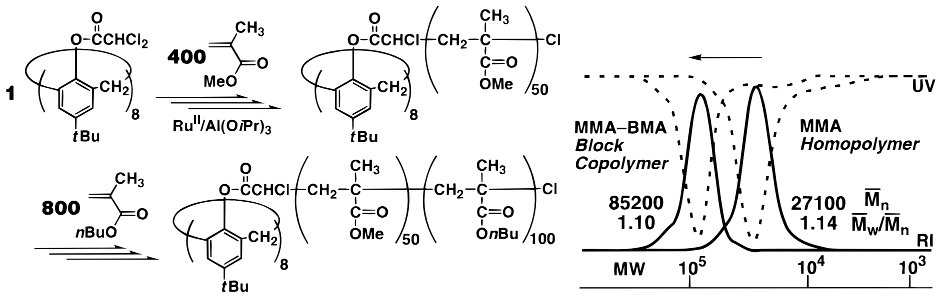

Figure 6. MWD curves of star poly(MMA) and star MMA–BMA block copolymers obtained with **4**/RuCl$_2$(PPh$_3$)$_3$/Al(O*i*Pr)$_3$ in toluene at 80 °C. $[\mathrm{MMA}]_0 = 0.50$ M; $[\mathbf{4}]_0 = 1.25$ mM; $[\mathrm{RuCl_2(PPh_3)_3}]_0 = 5.0$ mM; $[\mathrm{Al(O}i\mathrm{Pr)_3}]_0 = 20$ mM. The mole ratio of the monomers to **4**: MMA/BMA = 400/800. The DP$_n$ in the formulas are calculated values.

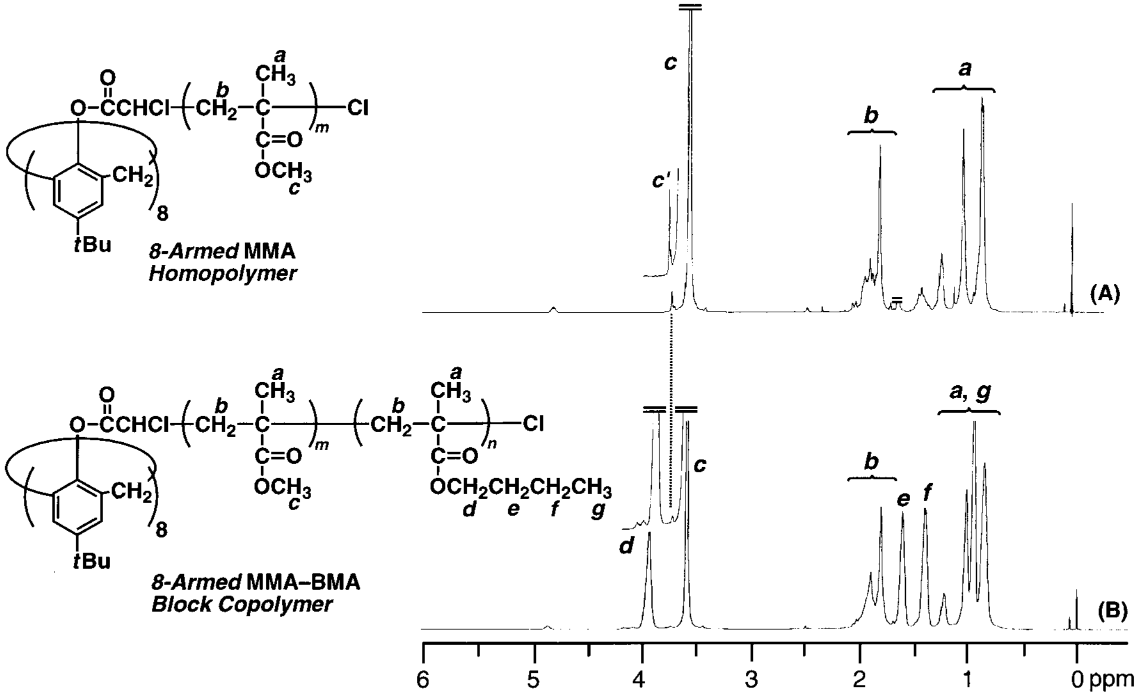

Figure 7. ^{1}H NMR spectra of star poly(MMA) and star MMA–BMA block copolymers with **4**/RuCl$_2$(PPh$_3$)$_3$/Al(O*i*Pr)$_3$ in toluene at 80 °C. $[\mathrm{MMA}]_0 = 0.50$ M; $[\mathbf{4}]_0 = 1.25$ mM; $[\mathrm{RuCl_2(PPh_3)_3}]_0 = 5.0$ mM; $[\mathrm{Al(O}i\mathrm{Pr)_3}]_0 = 20$ mM. The mole ratio of the monomers to **4**: MMA/BMA = 400/800.

sequential living polymerization of MMA and *tert*-butyl methacrylate.[1]

In conclusion, the calixarene-core initiators with four, six, and eight dichloroacetate units initiate living radical polymerization of MMA catalyzed by RuCl$_2$(PPh$_3$)$_3$ in the presence of Al(O*i*Pr)$_3$ to give tetra-, hexa-, and octaarmed star polymers, respectively. AB-block star copolymers of MMA and BMA were also prepared by sequential living polymerization initiated by the calixarene-core initiators.

Experimental Section

Synthesis of Monofunctional Initiator. Monofunctional ester **1** was prepared by the reaction between dichloroacetyl chloride and 4-*tert*-butylphenol. In a 500-mL round-bottomed flask filled with dry nitrogen, dichloroacetyl chloride (Wako Chemicals; purity >98%; 4.80 mL; 50 mmol) was added dropwise to a solution of 4-*tert*-butylphenol (Aldrich; purity >99%; 5.00 g; 33 mmol) and pyridine (6.03 mL; 67 mmol) in diethyl ether (70 mL). The reaction mixture was stirred at room temperature for 6 h and poured into 200 mL of deionized water. The aqueous phase was extracted with four 200-mL portions of diethyl ether, and the ether extracts were combined with the organic layer. The combined organic phase was washed with deionized water (300 mL) and dried with sodium sulfate overnight. It was then subjected to preparative size-exclusion chromatography (SEC) (column, Shodex H-2001; exclusion limit = 1 × 10^3; 2.5 cm i.d. × 50 cm) in chloroform. The purity of the isolated product (**1**) was confirmed by ^{1}H NMR (purity >98%; Figure 1A).

Synthesis of Tetrafunctional Initiator. Tetrafunctional ester **2** was obtained by the following method. Into a 500-mL round-bottomed flask filled with dry nitrogen was added *tert*-butyllithium (Aldrich; 1.7 M in pentane; 16.7 mL; 28.4 mmol) dropwise to a solution of 4-*tert*-butylcalix[4]arene (Tokyo Kasei; purity >98%; 3.68 g; 5.7 mmol) in toluene (100 mL) at −78 °C. The reaction mixture was slowly warmed to room temperature and stirred for 12 h. Dichloroacetyl chloride (16.6 mL; 175 mmol) was added dropwise to the solution, and the mixture was stirred at room temperature for an additional 12 h. It was poured into 300 mL of water, the aqueous phase was extracted with four 300-mL portions of chloroform, and the chloroform extracts were combined with the organic layer. The combined organic phase was washed with deionized water (300 mL) and dried with sodium sulfate overnight. After the chloroform was removed in vacuo, the crude products were recrystallized from CHCl$_3$/methanol (75:25) to give **2**: purity > 98% by ^{1}H NMR (Figure 1B).

Synthesis of Hexa- and Octafunctional Initiators. Hexafunctional ester **3** was prepared by the reaction between dichloroacetyl chloride and 4-*tert*-butylcalix[6]arene. Into a

500-mL round-bottomed flask filled with dry nitrogen was added dichloroacetyl chloride (4.87 mL; 50 mmol) dropwise to a solution of 4-*tert*-butylcalix[6]arene (Aldrich; purity >95%; 4.87 g; 5.0 mmol) and pyridine (6.03 mL; 75 mmol) in dimethylformamide (150 mL). After the mixture was stirred at room temperature for 24 h, it was poured into 300 mL of deionized water. The aqueous phase was extracted with four 300-mL portions of chloroform, and the chloroform extracts were combined with the organic layer. The combined organic phase was washed with deionized water (300 mL) and dried with sodium sulfate overnight. After the chloroform was removed by evaporation, the crude products were recrystallized from $CHCl_3$/methanol (75:25) to give **3**: purity >98% by ^1H NMR (Figure 1C). The octafunctional initiator, **4**, was also prepared and purified by similar methods: purity >98% by ^1H NMR (Figure 1D).

Other Materials. MMA (Tokyo Kasei; purity >99%) was dried over calcium chloride overnight and distilled twice over calcium hydride under reduced pressure before use. $RuCl_2(PPh_3)_3$ (Merck; purity >99%) and $Al(O\mathit{i}Pr)_3$ (Aldrich; purity >99.99%) 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 $Al(O\mathit{i}Pr)_3$ (0.1 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 **1** (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 (∼20 mL) and rigorously shaken with a solid, porous absorbent [Kyowaad-2000G-7 ($Mg_{0.7}Al_{0.3}O_{1.15}$); Kyowa Chemical] (∼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, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ 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 $= 5 \times 10^6$; 0.8 cm i.d. × 30 cm; flow rate = 1.0 mL/min; at 40 °C) 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; $\bar{M}_n = 630-220000$; $\bar{M}_w/\bar{M}_n = 1.06-1.22$) as well as the monomer. ^1H NMR spectra were recorded in $CDCl_3$ at 25 °C on a JEOL JNM-GSX270 spectrometer, operating at 270.7 or 500 MHz. Polymers for ^1H NMR analysis were fractionated by preparative SEC (column, Shodex K-2002; exclusion limit $= 5 \times 10^3$; 2.0 cm i.d. × 30 cm).

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References and Notes

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