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Multifunctional Coupling Agents for Living Cationic Polymerization. 3. Synthesis of Tri- and Tetraarmed Poly(vinyl ethers) with Tri- and Tetrafunctional Silyl Enol Ethers

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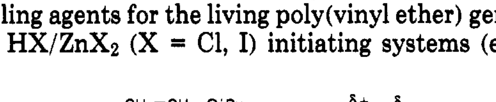
ABSTRACT: Tri- and tetrafunctional silyl enol ethers, $Me_{4-n}C[CH_2OC_6H_4C(OSiMe_3)=CH_2]_n$ (**3**: $n = 3$; **4**: $n = 4$), proved efficient multifunctional coupling agents for the living polymer of isobutyl vinyl ether (IBVE) prepared by the hydrogen chloride/zinc chloride ($HCl/ZnCl_2$) initiating system at -15 °C in methylene chloride. The silyl enol ethers were readily synthesized by the silyl enolation of the corresponding multifunctional acetophenones (*e.g.*, **6** and **8**). Upon the coupling reactions, the number-average molecular weights ($\bar{M}_n$) of the products increased in accordance with the multiplicity of the coupling agents (*e.g.*, 4-fold increase with **4**), while the molecular weight distributions became even narrower ($\bar{M}_w/\bar{M}_n < 1.1$) than that of the original living polymer. The products were identified by ^1H NMR spectroscopy; **3** and **4** led to the tri- and tetraarmed polymers (**3-P** and **4-P**, respectively), where the living polymer (arm) was connected to the coupling agent via an aromatic ketone linkage ($CH_2OC_6H_4COCH_2$-polymer). The coupling of a relatively short chain of living poly(IBVE) ($\overline{DP}_n \sim 10$) occurred nearly quantitatively to give the multiarmed polymers (yield > 95%), but the yield decreased slightly (85–90%) with a longer living chain ($\overline{DP}_n \sim 50$).

Introduction

Multiarmed polymers are interesting macromolecules with unique spatial shapes and have been synthesized in addition polymerization primarily by three methods:[1] (*i*) the living polymerization with a multifunctional initiator; (*ii*) the coupling reaction of linear living polymers with a multifunctional coupling agent (terminator); and (*iii*) the linking reaction of linear living polymers with a difunctional vinyl compound through microgel formation. In living cationic polymerization, the methods (*i*)[2] and (*iii*)[3] are already available, but few effective coupling agents for the method (*ii*) have been developed. Recently, we have indeed employed tri- and tetrafunctional malonate anions to this end, but their coupling reactions with living poly(vinyl ethers) were not efficient.[4] The major difficulty associated with the multifunctional malonate anions is the low solubility in organic solvents, along with the serious steric hindrance upon coupling three or four living chains onto a relatively small core. This led us to develop a new series of multifunctional coupling agents to afford multiarmed polymers more efficiently.

In the second paper of this series,[5] we have shown that silyl enol ethers are excellent quenching functions for coupling agents for the living poly(vinyl ether) generated with HX/ZnX_2 (X = Cl, I) initiating systems (eq 1). A selective and quantitative coupling reaction proceeds, as shown in eq 2, with a monofunctional silyl enol ether (*e.g.* **1**) that possesses an electron-donating group vicinal to the trimethylsiloxy group, to give the coupling product **1-P** where the living end is connected to an aromatic ketone moiety derived from the quencher. Consequently, the coupling of two living polymers by the corresponding bifunctional silyl enol ethers (*e.g.*, **2**) successfully give a chain-extended polymer (**2-P**) with a doubled molecular weight (eq 3).



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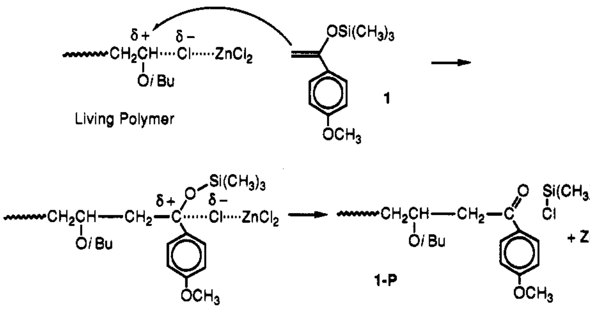

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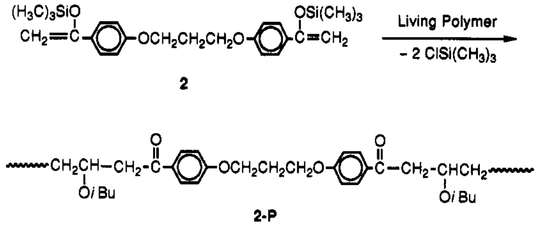

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In this study, we extended these findings to the synthesis of tri- and tetraarmed star polymers by the use of tri- and tetrafunctional silyl enol ethers (**3** and **4**, respectively) for the polymer coupling reactions (Schemes 1 and 2). According to our search of quenching groups for the HCl/$ZnCl_2$-initiated living polymer,[5] these multifunctional silyl enol ethers were designed to possess (a) the same enol ether functions as those in **1** and **2**, which have an electron-donating alkoxyphenyl group to enhance the reactivity of the double bond; and (b) a radially shaped, substituted methane core, along with the rigid phenyl spacers, both of which help the three and the four spatially well-separated enol ether moieties to minimize possible steric hindrance upon the coupling of three or four linear polymer chains. Also, despite their multifunctionalities, these silyl enol ethers **3** and **4** are, by definition, nonionic and ensure the high solubility in organic solvents for cationic polymerization.

This paper describes the synthesis of the multifunctional silyl enol ethers **3** and **4** and their reactions with living poly(vinyl ether)s into triarmed and tetraarmed polymers

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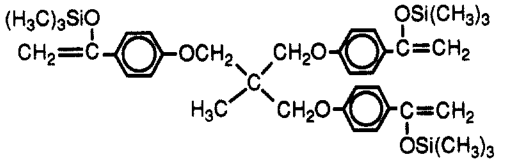

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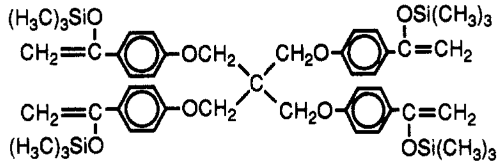

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with uniform and controlled arm lengths. These "inward" syntheses of multiarmed polymers via coupling reactions would be complementary to the "outward" counterparts via multifunctional initiators of living cationic polymerizations that we have already reported.[2c]

Results and Discussion

Synthesis of Tri- and Tetrafunctional Silyl Enol Ethers. Multifunctional silyl enol ethers 3 and 4 were synthesized by the two-step reactions, shown in Scheme 1, which consist of the etheration (step 1) of multifunctional alkyl halides (5 and 7) to the corresponding acetophenones (6 and 8, respectively) as the precursors; and the subsequent silyl enolation (step 2) of the ketone moieties (see Experimental Section for details).

The etheration of 5 and 7 (step 1) was carried out in a polar solvent (DMF or Me_2SO) in the presence of a base.[6] For example, 6 was afforded by the etheration of 1,3-dichloro-2-(chloromethyl)-2-methylpropane (5) and 3 equiv of 4-hydroxyacetophenone, and, similarly, 8 was prepared from pentaerythritol tetrabromide (7). The purification of the products yielded the tri- and tetrafunctional derivatives, the ^1H NMR spectra of which are shown in Figure 1A and Figure 2A (for 6 and 8, respectively). The spectra confirm the formation of 6 and 8.

The acetyl groups in 6 or 8 were subsequently transformed into silyl enol ethers with a silylating agent (Scheme 1, step 2). Among the many silylating agents reported,[7] we selected the trimethylchlorosilane/sodium iodide/triethylamine system, with which the quantitative silyl enolations of mono- and bifunctional acetophenones have been observed.[5,8]

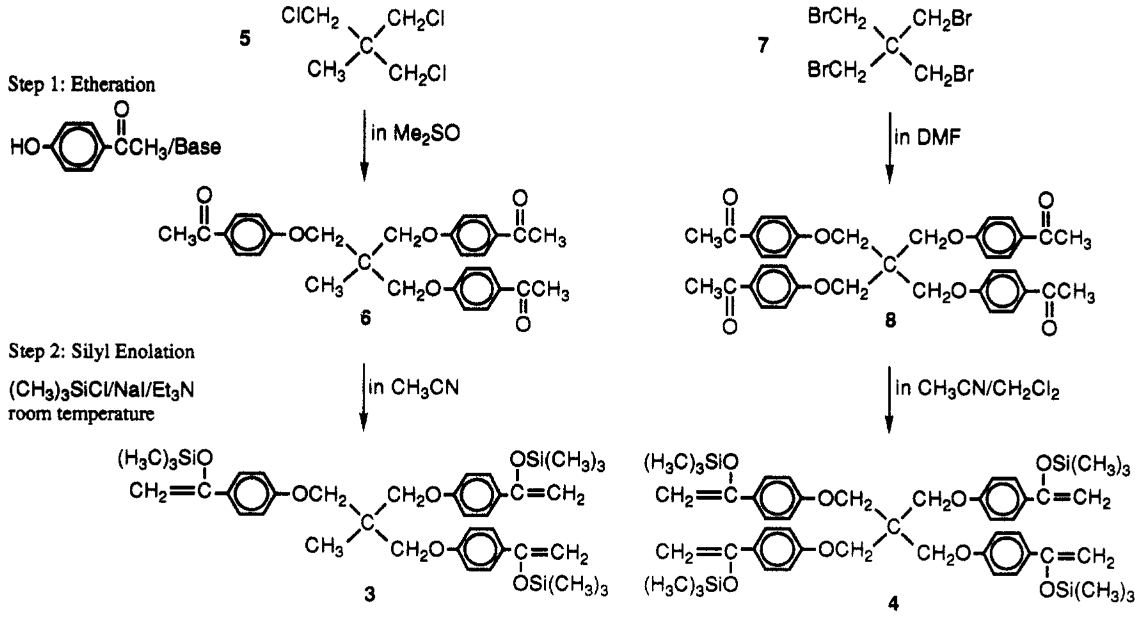
Thus, 6 and 8 were allowed to react with the silylating agent in acetonitrile and an acetonitrile/methylene chloride mixture, respectively, at room temperature under dry nitrogen; as the reaction proceeded, ammonium salts precipitated. Figure 1B and Figure 2B show the ^1H NMR spectra of the isolated products, which were handled under dry nitrogen. For example, before and after the silyl enolation of the trifunctional ketone 6 (Figure 1, parts A and B), the signal of the acetyl groups in 6 (spectrum A, signal e) disappeared, and, instead the signals of the double bond [(B) e] and the trimethylsiloxy group [(B) f] appeared. The aromatic protons, c and d, shifted upfield from 6.96 to 6.89 ppm (signal c) and from 7.93 to 7.50 ppm (signal d). Thus, the product was identified as trifunctional silyl enol ether 3. Similarly, the synthesis of the tetrafunctional silyl enol ether 4 was performed, as shown in Figure 2, parts A and B.

These results show the transformations of 6 and 8 to the silyl enol ethers (3 and 4) are feasible and quantitative without noticeable byproducts. The multifunctional enol ethers are highly soluble in polymerization solvents (*n*-hexane, toluene, methylene chloride, *etc.*), in sharp contrast to the multifunctional malonate anions, which are sparingly soluble therein.[9]

Synthesis of Tri- and Tetraarmed Poly(IBVE). The tri- and tetrafunctional silyl enol ethers, 3 and 4, were then employed as coupling agents for the living poly(IBVE) to synthesize the 3-arm and 4-arm star polymers (**3-P** and **4-P**, Scheme 2, respectively). For the coupling reactions, living poly(IBVE) was prepared with the $HCl/ZnCl_2$ initiating system in CH_2Cl_2 at −15 °C.[10] For comparison, the corresponding bifunctional silyl enol ether 2 was also employed under the same conditions.[5]

(a) Coupling Reactions with Short Chains of Living Poly(IBVE). For easy analysis of the structure and molecular weight of the products, relatively short living polymers ($\overline{DP}_n \sim 10$) were allowed to react with enol ethers 2–4. Thus, solutions of 2–4 in CH_2Cl_2 were added to the living poly(IBVE) (at IBVE conversion ~80%), and the reaction mixtures were kept at −15 °C for an additional 24 h with stirring. In these coupling reactions,

Scheme 1. Synthesis of Tri- and Tetrafunctional Silyl Enol Ethers



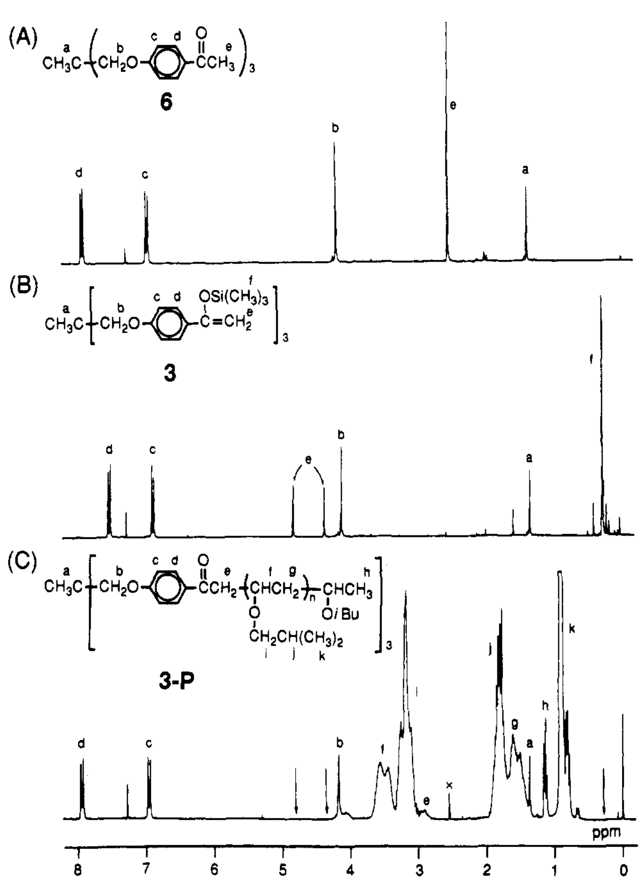


Figure 1. ^{1}H NMR spectra in the synthesis and polymer coupling of the trifunctional silyl enol ether **3** (*cf.* Schemes 1 and 2): (A) precursor **6**; (B) silyl enol ether **3**; (C) coupling product **3-P**.

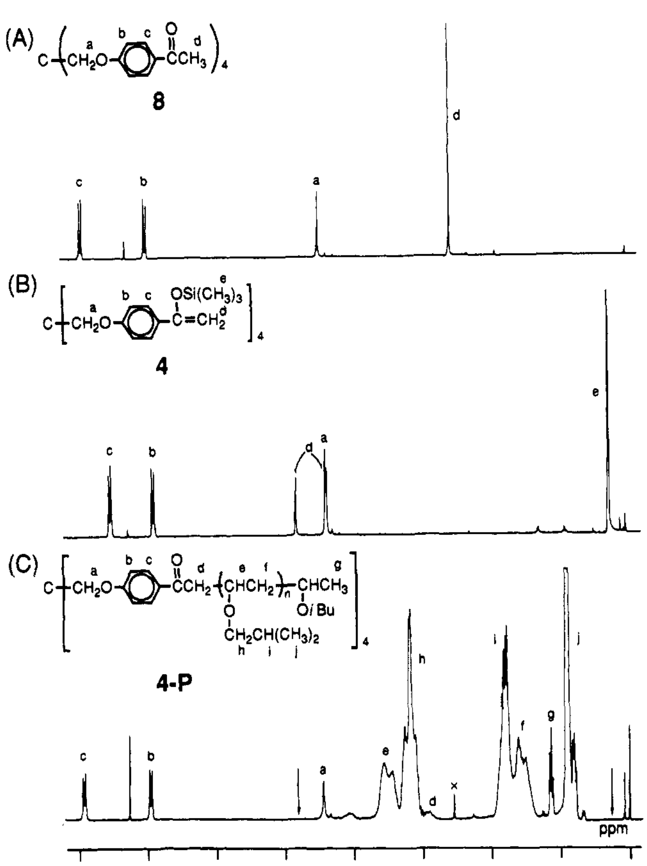


Figure 2. ^{1}H NMR spectra in the synthesis and polymer coupling of the tetrafunctional silyl enol ether **4** (*cf.* Schemes 1 and 2): (A) precursor **8**; (B) silyl enol ether **4**; (C) coupling product **4-P**.

by definition, the number of the silyl enol ether group must be identical to that of the living end in order to give the intended multiarmed polymers quantitatively, namely, [**2**]/[living end] = 1/2; [**3**]/[living end] = 1/3; [**4**]/[living end] = 1/4.

The molecular weight distributions (MWDs) of the coupled products are shown in Figure 3, parts B–D. In contrast to the original living polymer quenched with methanol (Figure 3A), the traces of the coupled products shifted toward higher molecular weights, where the extent of the shift was larger with increasing functionality of the coupling agents. The MWDs were narrow and without tails or minor peaks in the region where the original living polymer eluted. From these GPC analyses, the overall yields of the coupled products were above 95% (Table 1). The polydispersity ratios ($\bar{M}_w/\bar{M}_n$) were below 1.1, independent of the coupling agent's functionality (Table 1), although no corrections were made in calculating the ratios for the star-shaped structures of the products.

(b) Characterization of the Coupled Products. The structures of the coupled products (shown in Figure 3) were analyzed by ^{1}H NMR spectroscopy, and the results are summarized in Figures 1 and 2, as well as Table 1. Figure 1C and Figure 2C show the ^{1}H NMR spectra of the products obtained in the coupling reactions of the living poly(IBVE) with **3** and **4**, respectively. They are both consistent with the expected multiarmed polymers **3-P** and **4-P** (Scheme 2).

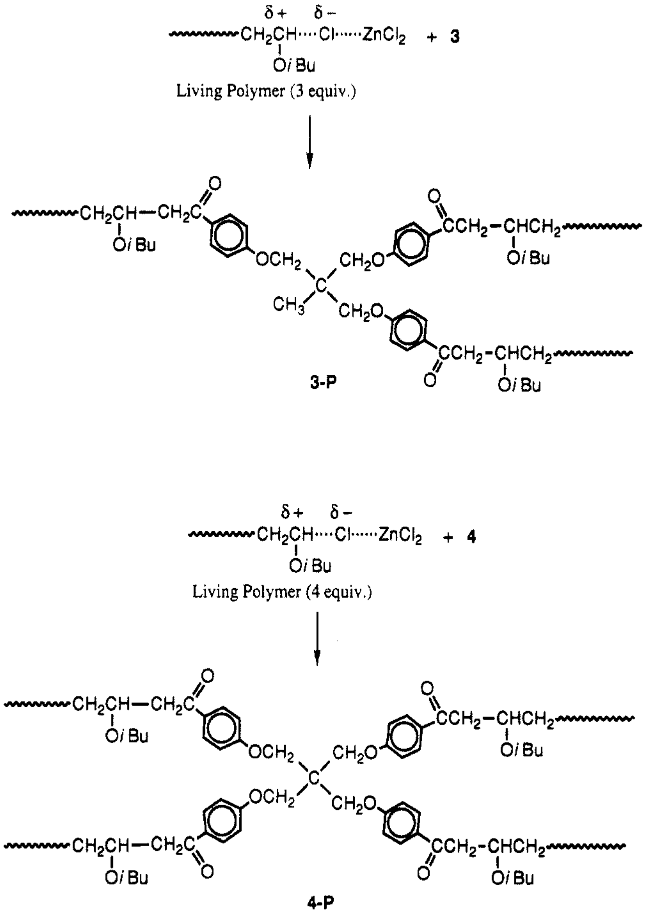
For example, upon the coupling reaction with the trifunctional silyl enol ether **3** (Figure 1B), the product (Figure 1C) showed the signals f–k for the poly(IBVE) chains along with peak h for the α-end methyl derived from the initiator (IBVE–HCl adduct);[10] the trimethylsilyloxy groups of the coupling agent [(B), signal f] disappeared completely; the enol ether methylene signals [(B), e] now appear as a broad multiplet around 3 ppm, and the aromatic protons (c and d) all shifted downfield to positions virtually the same as those of the precursor ketone **6** (Figure 1A), which are structurally very similar to the ketone of **3-P**.

Thus, the comparison among spectra A–C in Figure 1 demonstrates the nearly quantitative conversion of each enol ether group in **3** into the corresponding ketone by coupling with the living end. Although the small signal at 2.53 ppm in Figure 1C indicates the regeneration of the acetophenone-type acetyl group from a trace amount of the unreacted enol ether **3** during the workup with aqueous reagents, the byproduct is almost negligible. According to the integrated peak intensities for Figure 1C,[11] the mole ratio ($\bar{F}_n$) of the aromatic rings (peak c + d) in the core to the α-end methyl (peak h) in the arms was close to unity (entry 3, Table 1), also indicating the quantitative reaction of the silyl enol ether with the living end (or three arm chains per molecule).

Similarly, the spectral analysis summarized in Figure 2A–C confirmed the quantitative and clean coupling of **4** with four living chains into **4-P**. Thus, in the spectrum of the product (Figure 2C), the methyl signal of the silyl group [signal e, Figure 2B] is absent, and the aromatic resonances (signals b and c) are virtually identical to those of the precursor ketone (Figure 2A) having a similar aromatic moiety. The aromatic ring/α-methyl signal intensity ratio ($\bar{F}_n$)[11] was close to unity (entry 4, Table 1), showing the attachment of nearly four arm chains to the tetraketone core. Very similar results were obtained with the bifunctional coupling agent **2** (entry 2, Table 1).[5]

(c) Effects of Chain Length ($\overline{\mathrm{DP}}_n$). As shown in Figure 3E–H and Table 2, the coupling reactions with **2**–**4** were also carried out with longer living chains ($\overline{\mathrm{DP}}_n \sim 50$),

Scheme 2. Synthesis of Three- and Four-Armed Polymers with Multifunctional Coupling Agents



under the reaction conditions the same as for the shorter chains (with $HCl/ZnCl_2$ in CH_2Cl_2 at −15 °C for 24 h).

In contrast to the results with the shorter chains, the GPC profiles of the products showed bimodal distributions. The major fractions have narrow MWDs ($\bar{M}_w/\bar{M}_n < 1.1$) and molecular weights clearly higher than that of the starting living chain, in accordance with the functionality of the enol ether coupling agents. The minor fractions appear nearly at the same positions as the living chain. Thus, the major fractions are due to the coupling products (see below for structural verification), where the minor peaks come from the unreacted living chains. Nevertheless, the apparent yields of the coupling products are still high (85–90%, Table 2), slightly lower than those with the shorter chains (>95%, Table 1). The lower yields and the bimodal MWD indicate that the coupling reactions with longer chains are less efficient, most likely due to steric hindrance, although **3** and **4** are designed to have the three and four quenching sites spatially separated by the radially located aromatic spacers.

Despite the lower yields, the fractionated major products gave ^1H NMR spectra very similar to those in Figures 1 and 2, and they are the products **2-P**–**4-P**. As shown in Table 2, each arm is connected to the aromatic ketone ($\bar{F}_n \sim 1.0$), and any unreacted silyl enol ether was nearly absent.

Conclusions. The tri- and tetrafunctional silyl enol ethers, **3** and **4**, are found to be soluble and efficient coupling agents for the living poly(IBVE) initiated with $HCl/ZnCl_2$. For short living chains, the coupling reactions were nearly quantitative to afford three-armed and four-armed star polymers (**3-P** and **4-P**, respectively) with uniform arm lengths and narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n < 1.1$). Thus, as multifunctional coupling agents, the silyl enol ethers are superior to the corresponding malonate anions,[5] which suffer from much lower yields of multiarmed polymers.

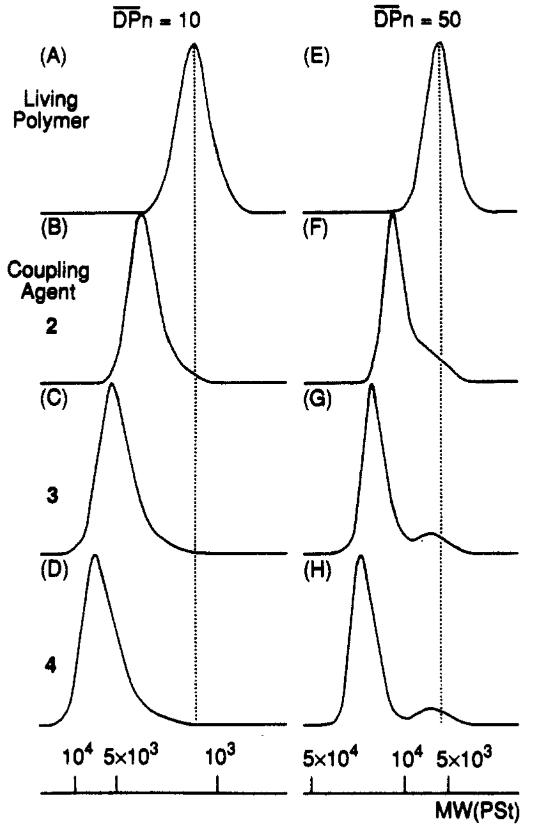


Figure 3. GPC curves of the products obtained by the coupling reactions of the $HCl/ZnCl_2$-initiated living polymer [$\overline{DP}_n \sim 10$ (A), 50 (E)] with the bi-, tri-, and tetrafunctional silyl enol ethers in CH_2Cl_2 at −15 °C for 24 h (*cf.* Scheme 2). Coupling agents: (B and F) **2**; (C and G) **3**; (D and H) **4**. See Tables 1 and 2 (both footnote *a*) for the reaction conditions.

Experimental Section

Materials. (a) Reagents. *n*-Hexane, CH_2Cl_2, and CCl_4 (solvents) and isobutyl vinyl ether (monomer) were washed by the usual methods[12] and distilled over calcium hydride (CaH_2) at least twice before use. Diethyl ether (Dojin, anhydrous) was distilled over lithium aluminum hydride before use. Zinc chloride (Aldrich, 1.0 M in diethyl ether) was used as received and diluted with diethyl ether to be at a given concentration. The IBVE–HCl adduct (initiator; 1.0 M *n*-hexane solution) was prepared as reported.[10b]

(b) Coupling Agents. 1,3-Bis{*p*-[1-[(trimethylsilyl)oxy]vinyl]phenoxy}propane (**2**) was prepared as reported.[5] Tri- and tetrafunctional silyl enol ethers (**3** and **4**, respectively) were synthesized as described below. The concentrations of these coupling agents in stock solutions in CH_2Cl_2 were determined by ^1H NMR with 1,3,5-trimethoxybenzene as the internal standard. Namely, the ^1H NMR spectrum was taken for a mixture of a solution of the silyl enol ether (0.50 mL in CH_2Cl_2) and the standard solution of the benzene (0.50 mL; 113.6 mM in CCl_4); an acetone-d_6 capillary cell was used for the external lock signal. The concentrations were then determined from the peak intensity ratio of the aromatic protons.

(c) Synthesis of 1,1,1-Tris{[*p*-[1-[(trimethylsilyl)oxy]vinyl]phenoxy]methyl}ethane (3). This trifunctional silyl enol ether was synthesized from 1,1,1-tris{[*p*-acetylphenoxy]methyl}ethane (**6**) (Scheme 1). In a 300-mL round-bottom flask, 4-hydroxyacetophenone (25 g, 0.18 mol) in Me_2SO (40 mL) was added dropwise to a mechanically stirred dispersion of potassium carbonate (20 g, 0.15 mol) in Me_2SO (60 mL) at room temperature. 1,3-Dichloro-2-(chloromethyl)-2-methylpropane (**5**; 8.47 mL, 0.061 mol) and 18-crown-6 (5.0 g, 0.019 mol) were added, and the solution was stirred at room temperature for 30 min and then at 135 °C for 4 days. The mixture was cooled to room temperature

Table 1. Coupling Reactions of Living Poly(IBVE) ($\overline{\mathrm{DP}}_n$ ~ 10) with Bi-, Tri-, and Tetrafunctional Silyl Enol Ethers 2–4[a]

						$\bar{M}_n \times 10^{-3}$		
entry	coupling agent	$\bar{F}_n$[b] (^{1}H NMR)	$\bar{N}$ (arm)[c]	% yield (GPC)	$\overline{\mathrm{DP}}_n$ (arm) (^{1}H NMR)[d]	^{1}H NMR[e]	GPC	$\bar{M}_w/\bar{M}_n$ (GPC)
1	MeOH		1.00		13.0	1.3	1.4	1.08
2	**2**	1.07	2.14	>95	14.6	3.4	2.9	1.07
3	**3**	1.01	3.03	>95	15.3	5.1	5.2	1.09
4	**4**	0.99	3.96	>95	14.9	6.5	6.1	1.09

[a] Coupling reaction conditions: [living polymer]/[**2**] = 2.0; [living polymer]/[**3**] = 3.0; [living polymer]/[**4**] = 4.0; in CH_2Cl_2 at −15 °C for 24 h. Polymerization conditions: $[IBVE]_0$ = 150 mM; $[IBVE–HCl\ adduct]_0$ = 10 mM; $[ZnCl_2]_0$ = 0.20 mM; in CH_2Cl_2 at −15 °C for 15 min; conversion ~ 80%; $\overline{\mathrm{DP}}_n$ (calcd) = 12.8. See Figure 3A–D and Figure 1. [b] $\bar{F}_n$ = (α-end CH_3)/(the phenyl groups), by ^{1}H NMR; $\bar{F}_n$ (theory) = 1.00; see also ref 11. [c] The number of arms per polymer: $\bar{N}$ (arm) = $\bar{F}_n$ × (the number of silyl enol ethers per coupling agent). [d] $\overline{\mathrm{DP}}_n$ shows the degree of polymerization of the arm polymer by ^{1}H NMR. [e] $\bar{M}_n$ (^{1}H NMR) = $\bar{N}$ (arm) × $\overline{\mathrm{DP}}_n$ (^{1}H NMR) × (mol wt of IBVE) + (mol wt of the coupling agent).

Table 2. Coupling Reactions of Living Poly(IBVE) ($\overline{\mathrm{DP}}_n$ ~ 50) with Bi-, Tri-, and Tetrafunctional Silyl Enol Ethers 2–4[a]

						$\bar{M}_n \times 10^{-4}$		
entry	coupling agent	$\bar{F}_n$[b] (^{1}H NMR)	$\bar{N}$ (arm)[c]	% yield (GPC)	$\overline{\mathrm{DP}}_n$ (arm) (^{1}H NMR)[d]	^{1}H NMR[e]	GPC	$\bar{M}_w/\bar{M}_n$ (GPC)
1	MeOH		1.00		43.6	0.44	0.53	1.05
2[f]	**2**	1.00	2.00	86	54.4	1.1	1.2	1.05
3[f]	**3**	0.99	2.97	86	46.5	1.4	1.6	1.03
4[f]	**4**	0.93	3.72	89	47.6	1.8	1.9	1.04

[a] Coupling reaction conditions: [living polymer]/[**2**] = 2.0; [living polymer]/[**3**] = 3.0; [living polymer]/[**4**] = 4.0; in CH_2Cl_2 at −15 °C for 24 h. Polymerization conditions: $[IBVE]_0$ = 500 mM; $[IBVE–HCl\ adduct]_0$ = 10 mM; $[ZnCl_2]_0$ = 0.20 mM; in CH_2Cl_2 at −15 °C for 40 min; conversion ~ 93%. See Figure 3E–H. [b] $\bar{F}_n$ = (α-end CH_3)/(the phenyl groups), by ^{1}H NMR; $\bar{F}_n$ (theory) = 1.00; see also ref 11. [c] The number of arms per polymer: $\bar{N}$ (arm) = $\bar{F}_n$ × (the number of silyl enol ethers per coupling agent). [d] $\overline{\mathrm{DP}}_n$ shows the degree of polymerization of the arm polymer by ^{1}H NMR. [e] $\bar{M}_n$ (calcd) = $\bar{N}$ (arm) × $\overline{\mathrm{DP}}_n$ (^{1}H NMR) × (mol wt of IBVE) + (mol wt of the coupling agent). [f] For the samples fractionated by preparative GPC from the products shown in Figure 3F–H.

and extracted with CH_2Cl_2 (3 × 200 mL). The combined CH_2Cl_2 phase was washed with aqueous 5% NaOH (300 mL) and water (3 × 300 mL) and dried over anhydrous sodium sulfate overnight. The CH_2Cl_2 was evaporated off under reduced pressure to give oily products, which were dissolved in acetone/*n*-hexane (1:1 v/v). The solution was passed through a silica gel column (2.5 cm i.d. × 15 cm) and evaporated to dryness under reduced pressure. The solid residue was purified by preparative gel permeation chromatography (Shodex H2001; exclusion limit = 1 × 10^3; 2.5 cm i.d. × 50 cm) in chloroform to give the precursor **6** as a solid (1.0 g, yield 3.1% from **5**). The ^{1}H NMR spectrum is shown in Figure 1A.

In a 100-mL, nitrogen-filled, baked flask equipped with a three-way stopcock and a magnetic stirrer bar was prepared a solution of **6** (0.66 g, 0.0014 mol), sodium iodide (8.4 mL of a 0.6 M solution in acetonitrile), and triethylamine (0.7 mL, 0.005 mol) in acetonitrile (4.0 mL). Trimethylchlorosilane (0.63 mL, 0.005 mol) was added dropwise via a dry syringe at room temperature with stirring.[5,8] The mixture was stirred for 2 h, and the low-boiling substances like acetonitrile were evaporated off under dry nitrogen. The residue was diluted with dry *n*-hexane (30 mL), and the precipitating ammonium salt was removed by three filtrations under dry nitrogen through a HPLC disk filter (0.50-μm pore). The filtered solution was evaporated under reduced pressure to give **3** as a yellowish oil, whose ^{1}H NMR ($CDCl_3$) was shown in Figure 1B. Since the acetyl groups in **6** were nearly quantitatively converted into silyl enol ethers (>99% by ^{1}H NMR), the as-obtained oil was weighed, dissolved in CH_2Cl_2 (22 mL) without further purification ([**3**] = 56.1 mM), and stored in ampoules under dry nitrogen in a freezer (−25 °C) until used.

(d) Synthesis of Pentaerythritol Tetrakis{*p*-[1-[(trimethylsilyl)oxy]vinyl]phenyl} Ether (4). This tetrafunctional silyl enol ether was synthesized from pentaerythritol tetrakis(*p*-acetylphenyl) ether (**8**) (Scheme 1). In a 500-mL round-bottom flask, 4-hydroxyacetophenone (25 g, 0.18 mol) in DMF (60 mL) was added dropwise to a mechanically stirred solution of sodium hydroxide (10.5 g, 0.26 mol) in DMF (40 mL) at room temperature. The mixture was warmed to 70 °C in a water bath, pentaerythritol tetrabromide (**7**; 17.5 g, 0.045 mol) in DMF (170 mL) was added, and the solution was stirred for an additional 9 h at 70 °C. The mixture was then extracted with CH_2Cl_2 (3 × 150 mL) and dried in the same way as for **6**. The CH_2Cl_2 was evaporated off under reduced pressure to give a solid. Because ^{1}H NMR analysis indicate that the conversion from CH_2Br to $CH_2OC_6H_4$-*p*-$C(O)CH_3$ was 66%,[6] and additional amount of the acetophenone was added to complete the etheration. Thus, in a 200-mL round-bottom flask, a solution of the product in DMF (20 mL) was added to a mixture of 4-hydroxyacetophenone (7.16 g, 0.053 mol) and sodium hydride (3.1 g, 0.078 mol; 60 wt % dispersion in mineral oil) in DMF (40 mL), and the mixture was stirred at 100 °C for 7 h. The products were separated and purified as for **6**, to give the precursor **8** as a solid (2.7 g, yield 10% from **7**). ^{1}H NMR ($CDCl_3$) is shown in Figure 2A.

In a 100-mL, nitrogen-filled, baked flask, equipped with a three-way stopcock and a magnetic stirrer bar, was prepared a solution of **8** (1.3 g, 0.0022 mol), sodium iodide (16.2 mL, 0.6 M in acetonitrile), and triethylamine (1.35 mL, 0.0097 mol) in an acetonitrile/CH_2Cl_2 mixture (10/5 mL). Trimethylchlorosilane (1.23 mL, 0.0097 mol) was added dropwise via a dry syringe at room temperature with stirring,[5,8] and the mixture was stirred for 2 h. After the extraction and filtration as for **3** (see above), the extract was evaporated under reduced pressure to give **4** as a solid, whose ^{1}H NMR ($CDCl_3$) was shown in Figure 2B. Since the acetyl groups in **8** were nearly quantitatively converted into silyl enol ethers (>99% by ^{1}H NMR), the as-obtained solid was weighed, dissolved in CH_2Cl_2 (20 mL) ([**4**] = 41.4 mM), and stored in ampoules under dry nitrogen in a freezer (−25 °C) until used.

Procedures. (a) Polymerization and Coupling Reactions. Living cationic polymerization of IBVE was carried out under dry nitrogen in a 50-mL baked flask equipped with a three-way stopcock with magnetic stirring.[5] A mixture of IBVE (0.2 mL), CCl_4 (0.2 mL, internal standard for GC analysis), and CH_2Cl_2 (7.6 mL) was cooled to −15 °C, and solutions of the IBVE–HCl adduct (1.0 mL; 0.10 M in *n*-hexane) and $ZnCl_2$ (1.0 mL; 2.0 mM in diethyl ether) were added in order. A living polymer ($\overline{\mathrm{DP}}_n$ ~ 10; [living end] = 10 mM) was formed in a near quantitative yield after 15 min. The living polymer of a longer chain length ($\overline{\mathrm{DP}}_n$ ~ 50; [living end] = 10 mM) was prepared similarly, under the conditions shown in footnote *a*, Table 2.

To these living polymer solutions (10 mL) kept at −15 °C, the CH_2Cl_2 solution of the coupling agent at room temperature was quickly added with vigorous stirring. The amounts of the added coupling agent solutions were determined so as to maintain the stoichiometry ([living end] = [silyl enol ether group]) as closely as possible (*i.e.* **2**, 1.0 mL of a 50.0 mM solution; **3**, 0.59 mL of a 56.1 mM solution; **4**, 0.60 mL of a 41.4 mM solution). The mixture was stirred at −15 °C for an additional 24 h, washed three times with water (30 mL), evaporated to dryness under reduced pressure, and finally vacuum-dried to give the coupled polymer. The samples of ^{1}H NMR analysis were separated by preparative gel permeation chromatography (Shodex K2003; exclusion limit = 7×10^4; 2.5 cm i.d. × 30 cm).

(b) Polymer Characterization. Gel permeation chromatography was carried out in chloroform on a Jasco Trirotar-II chromatograph equipped with polystyrene gel columns (Shodex K-802, K-803 and K-804; exclusion limit = 4×10^5; 8.0 mm i.d. × 30 cm each) and refractive index/ultraviolet dual-mode detectors. The number-average molecular weight ($\bar{M}_n$) and the MWD of the polymers were determined on the basis of polystyrene standard samples. ^{1}H NMR spectra (270 MHz) were recorded on a JEOL GSX-270 at room temperature.

References and Notes

(1) The multiarmed (star-shaped or star-branched) polymers have been prepared by living anionic polymerization; see, for example: (a) Bauer, B. J.; Fetters, L. J. *Rubber Chem. Technol.* **1978**, *51*, 406. (b) Bywater, S. *Adv. Polym. Sci.* **1979**, *30*. 89. (c) Morton, M. *Anionic Polymerization: Principles and Practice*; Academic Press: London, 1983.

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(6) Monitoring the reactions by ^{1}H NMR spectroscopy showed the progress of the etheration. The signals of the halogenated methylene protons, 3.68 (CH_2Cl in **5**) or 3.59 ppm (CH_2Br in **7**), disappeared with the reaction, and new signals, 4.17 (for **6**) or 4.42 ppm (for **8**), were observed, respectively.

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(9) The homogeneous solution of a bifunctional malonate anion was obtained in a THF/crown ether mixture, but the as-prepared solutions of tri- and tetrafunctional malonate anions contained insoluble parts whose amount increased on standing.[4]

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(11) For **3-P** (Figure 1C), $\bar{F}n = (h/3)/[(c + d)/2]$; for **4-P** (Figure 2C), $\bar{F}n = (g/3)/[(b + c)/2]$.

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