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Multifunctional Coupling Agents for Living Cationic Polymerization. 2. Bifunctional Silyl Enol Ethers for Living Poly(vinyl ethers)

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ABSTRACT: Bifunctional silyl enol ethers, specifically 1,3-bis{*p*-[1-[(trimethylsilyl)oxy]vinyl]phenoxy}propane (**5**), 1,4-diethoxy-1,4-bis[(trimethylsilyl)oxy]-1,3-butadiene (**6**), and 2,4-bis[(trimethylsilyl)oxy]-1,3-pentadiene (**7**), are highly soluble and efficient bifunctional coupling agents for the living polymers of isobutyl vinyl ether (IBVE) initiated with hydrogen chloride/zinc chloride ($HCl/ZnCl_2$) at −15 °C in methylene chloride and toluene solvents. The products are linear poly(IBVE) with molecular weights twice those of the starting living chains and with molecular weight distributions are narrow as those of the precursors. NMR structural analysis of the products shows the coupling reaction to involve an electrophilic addition of the living end onto the enol ether double bond of the coupling agent to form a ketone with the formation of trimethylsilyl chloride. In particular, the bifunctional enol ether **5**, bearing a highly electron-donating substituent at the α-carbon of the silyl enol ether, leads to a nearly quantitative coupling reaction (yield >95%) for a relatively short living poly(IBVE) ($\overline{DP}_n \sim 10$). The other two coupling agents, **6** and **7**, also gave high coupling yields above 90%. By contrast, a similar but vicinal bis(enol ether), 2,3-bis[(trimethylsilyl)oxy]-1,3-butadiene (**8**), failed to undergo such a coupling reaction under the same conditions. The coupling efficiency thus depends on the silyl enol ether structure and also the chain length of the living poly(IBVE); i.e., more coupling occurs with shorter chains. Model quenching reactions with the corresponding monofunctional silyl enol ethers [e.g., *p*-methoxy-α-[(trimethylsilyl)oxy]styrene (**1**) for **5**] show the importance of electron-donating α-substituents on coupling agents that increase the electron density of the enol ether double bond.

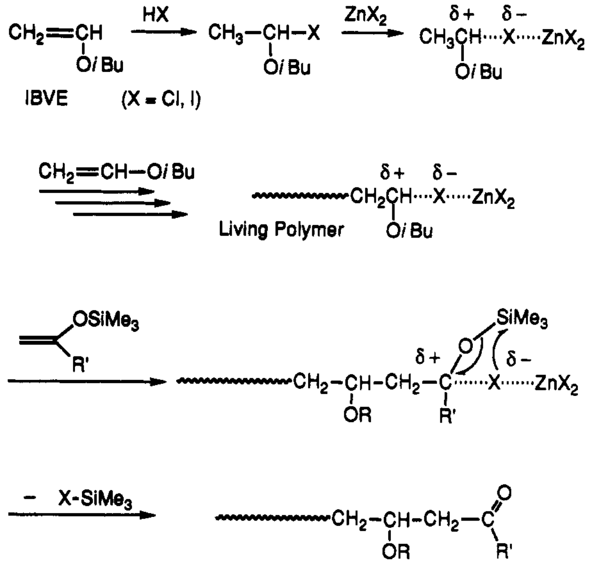
Introduction

Recently we began a series of studies to develop multifunctional coupling agents (terminators) for living cationic polymerization of vinyl monomers. In the first report of this series,[1] we employed bis- to tetrakis(malonate) anions ($C_6H_{6-n}[CH_2C^-(COOEt)_2Na^+]_n$; n = 2–4) for coupling living poly(vinyl ethers) initiated with hydrogen iodide/zinc iodide (HI/ZnI_2). The bifunctional malonate salt (n = 2), in principle, is useful in combining two chains of the living poly(vinyl ether) to give chain-coupled products, ABA block copolymers, and end-functionalized polymers.

In contrast to their monofunctional counterpart [Na^+ $^-CH(COOEt)_2$],[2] these multiple anions are less soluble in polymerization solvents such as toluene and methylene chloride and thus require precise control of reaction conditions for the quantitative coupling to proceed. For example, the bis(malonate) anion had to be dissolved in tetrahydrofuran containing a crown ether to form a solution, in which a clean, fast, and quantitative coupling occurred. Even under these conditions, the tri- and tetraanions (n = 3, 4) are less efficient coupling agents, probably because of low solubility and sterically hindered coupling sites. Thus the synthesis of tri- and tetraarmed polymers is incomplete.

These results led us to explore "nonionic" nucleophiles, which are expected to be soluble in organic solvents and to be more efficient multiple coupling agents for living cationic polymers. Thus, in this study, silyl enol ethers were studied as nonionic nucleophiles that would undergo quantitative coupling reactions in living cationic polymerization (Scheme I). Trialkylsilyl enol ethers are known to react with carbocations to form a carbon–carbon bond with the liberation of a trimethylsilyl group.[3] More recently, McGrath and Riffle used a silyl enol ether (trimethylsilyl ketene acetal) to terminate the HI/ZnI_2-initiated living poly(vinyl ether).[4] However, the suitability and scope of nonionic nucleophiles like silyl enol ethers for chain-coupling reactions in living cationic polymerization are unknown; no multiple silyl enol ether has yet been studied as a multifunctional coupling agent.

Scheme I. Living Polymer Quenched with Silyl Enol Ether



This study has the following two objectives: (i) to identify silyl enol ethers that can undergo fast and quantitative 1:1 coupling reactions with living poly(vinyl ethers) and, on the basis of this screening, (ii) to design bifunctional silyl enol ethers as new bifunctional coupling agents for living cationic polymers. Because of the high affinity of halogen anions toward trialkylsilyl groups,[5] HX/ZnX_2 (X = I, Cl) initiating systems[6,7] were chosen to obtain

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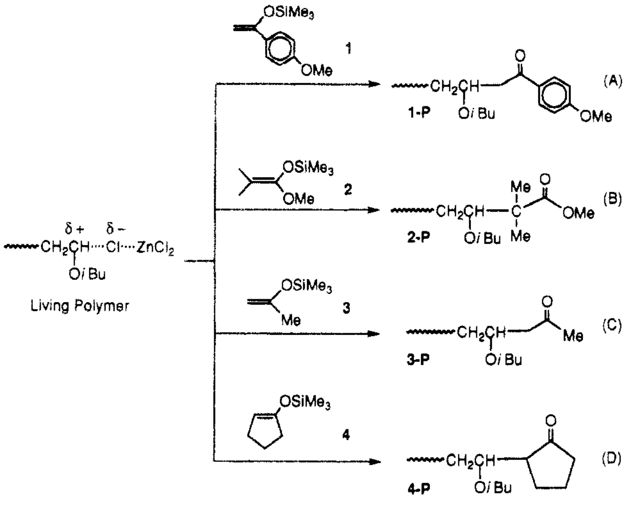
Scheme II. Model Coupling Reactions with Silyl Enol Ethers



living poly(isobutyl vinyl ether) [poly(IBVE)] for coupling experiments.

Results and Discussion

Model Reactions with Monofunctional Silyl Enol Ether Coupling Agents and Poly(IBVE). A multifunctional coupling agent for a living polymer must be able to undergo a fast and quantitative coupling reaction on an equimolar basis when the [functional group]/[living end] = 1. As shown in Scheme II, a series of monofunctional silyl enol ethers (1–4) were allowed to react with a living poly(IBVE) formed by the HCl/$ZnCl_2$ initiating system in CH_2Cl_2 at −15 °C. The initiator used was the adduct of IBVE with hydrogen chloride prepared separately and identified.[7a] Thus, when IBVE monomer was almost completely polymerized in this way to ca. 95% conversion, enol ethers 1–4 were added to solutions of the living poly(IBVE), and the reaction mixtures were stirred in CH_2Cl_2 at −15 °C for an additional 30 min. In these model coupling reactions, the degree of polymerization ($\overline{DP}_n$) of the living chain was made deliberately low ($\overline{DP}_n$ ~ 10) to simplify analysis of the structure and molecular weight of the products. The silyl enol ethers were added in slight molar excess (1.2 equiv) over the living end. The results are summarized in Figure 1 and Table I.

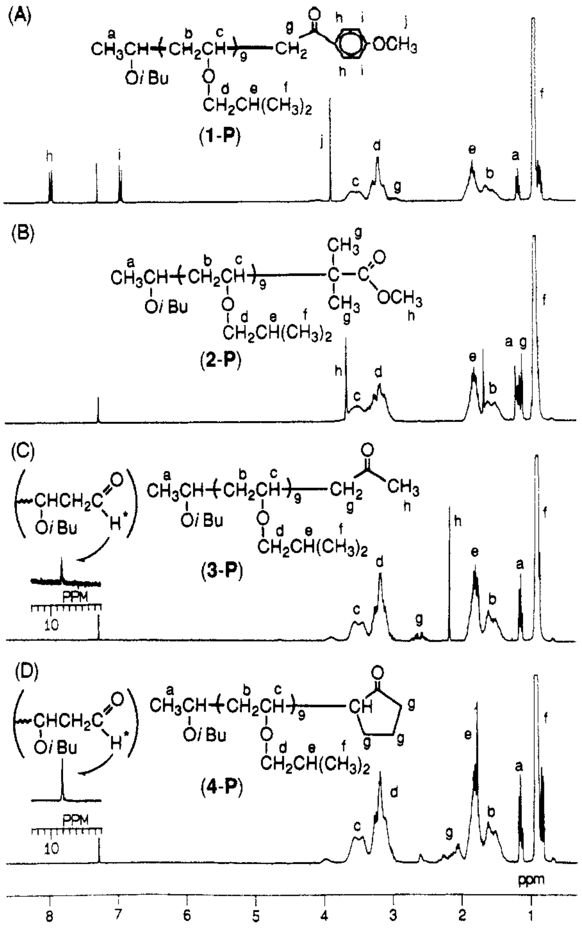
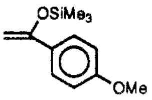
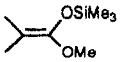
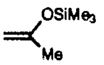
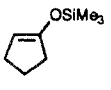


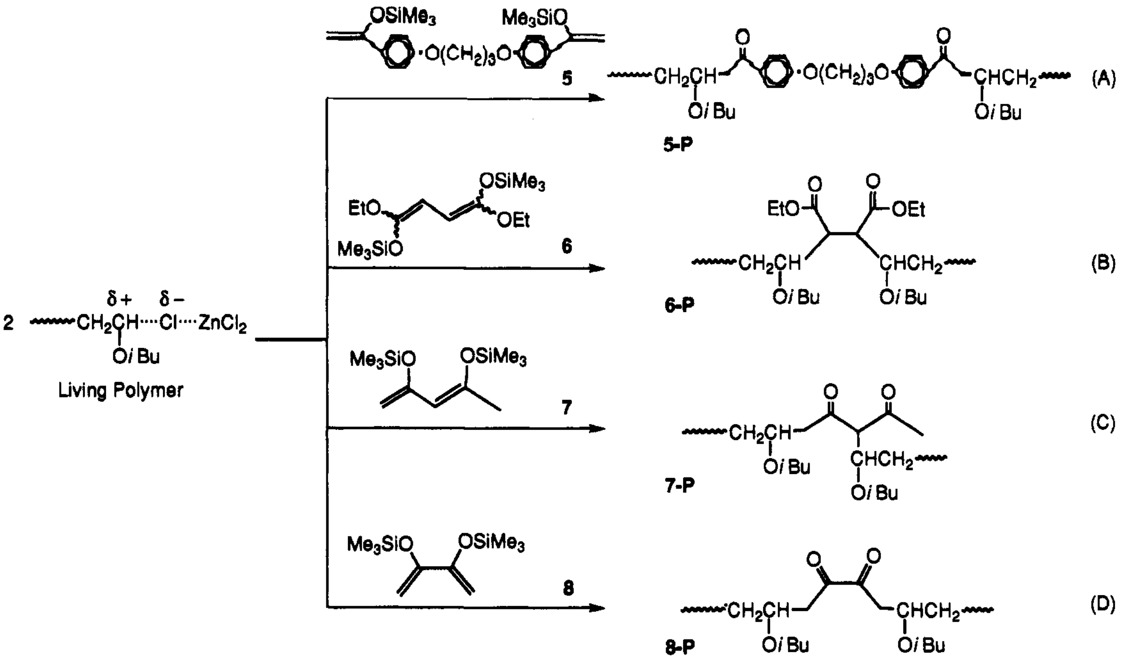
Figure 1. ¹H NMR spectra ($CDCl_3$, room temperature) of the coupling products obtained in the model reactions with silyl enol ethers 1–4 in CH_2Cl_2 at −15 °C for 30 min (cf. Scheme II and Table I): (A) 1-P; (B) 2-P; (C) 3-P; (D) 4-P. The insets in C and D show the aldehyde group at the ω-end of the polymer from the reaction of the living polymer with wash water after the model reaction.

Table I. Model Coupling Reactions of Silyl Enol Ethers with Living Polymer[a]

				$\overline{DP}_n$		$\overline{M}_n$		$\overline{M}_w/\overline{M}_n$	$\overline{F}_n$[c]
entry	coupling agent	δ($C^β$),[b] ppm	δ($C^α$),[b] ppm	calcd	¹H NMR	GPC	¹H NMR	GPC	¹H NMR
	MeOH			9.5		1016		1.06	
1	 1	89.3	155.3	9.5	9.3	990	1080	1.09	1.00
2	 2	90.6	149.3	9.5	9.9	930	1090	1.06	1.03
3	 3	91.2	155.9	9.5	8.6	980	920	1.07	0.79
4	 4	101.9	154.9	9.5	9.0	900	990	1.07	0.67

[a] Polymerization conditions: $[IBVE]_0$ = 90 mM; $[IBVE–HCl\ adduct]_0$ = 10 mM; $[ZnCl_2]_0$ = 1.0 mM; in CH_2Cl_2 at −15 °C for 5 min; conversion = 94%; $\overline{DP}_n$ = 8.5 + 1.0 (from the adduct) = 9.5. Coupling reaction conditions: $[coupling\ agent]_0/[living\ polymer]_0$ = 1.2 at −15 °C for 30 min. [b] ¹³C NMR chemical shifts of the α- and β-carbons of silyl enol ethers: $C^β{=}C^αOSiMe_3$. [c] The number of enoalte-derived ends per polymer (see Figure 1): $\bar{F}_n$ = (ω-end)/(α-end).

Scheme III. Coupling Reactions with Bifunctional Silyl Enol Ethers



All of the polymers thus obtained had narrow molecular weight distributions (MWDs) ($\overline{M}_w/\overline{M}_n \sim 1.1$), which were virtually unchanged compared with that of the living polymer quenched with methanol (Table I). The ^{1}H NMR spectra (Figure 1) of the products invariably exhibited the signals of the terminal methyl group (α-end) which originated from the initiator (IBVE–HCl adduct) (signal a, 1.2 ppm) and the pendant methyl groups of the IBVE units (signal f, 0.9 ppm), and their intensity ratio [(f/6)/(a/3)] agreed well with the calculated value based on the monomer/initiator feed mole ratio and the conversion.

In addition to these signals, the poly(IBVE) chains of each product showed absorptions due to another terminal group (ω-end) derived from the enol ether quencher. As shown in Figure 1, these resonances with peak assignments include 1 (Figure 1A), g–j; 2 (Figure 1B), g and h; 3 (Figure 1C), g and h; 4 (Figure 1D), g. The detection of these signals demonstrates that all four enol ethers can quench the living poly(IBVE) to give the expected end-capped polymers (**1-P**–**4-P**, Scheme II) where the added enol ethers are attached to the ω-ends as carbonyl moieties. From the signal intensity ratios of these terminal groups to the α-end methyl (peak a), the number-average end functionality ($\bar{F}_n$) of the products **1-P**–**4-P** was determined (Table I).[8] The end functionality of the chains depends on the structure of the enol ether quenchers.

For the silyl enol ethers 1 and 2 which carry a strongly electron-donating substituent geminal to the silyloxy group (Table I, entries 1 and 2), the end group functionalities ($\bar{F}_n$) were very close to unity, indicating the quantitative attachment of the enol ethers. In contrast, for the silyl enol ethers 3 and 4 with less electron-donating substituents (Table I, entires 3 and 4), the $\bar{F}_n$ was clearly below unity. As seen in Figure 1C,D, the products with 3 and 4 showed additional low-field signals at 9.82 ppm that are assignable to the terminal aldehyde group (CH*=O). This aldehyde is formed most likely via the reaction of the living end with water during the workup, followed by the elimination of isobutyl alcohol from the resulting hemiacetal; i.e., $\sim\sim\sim CH_2CH^{\delta+}(OiBu)\cdots Cl^{\delta-}\cdots ZnCl_2 + H_2O \rightarrow \sim\sim\sim CH_2CH(OiBu)OH \rightarrow \sim\sim\sim CH_2CH{=}O$.[9] The decomposition of the living end during the workup indicates that the termination processes with 3 and 4 were rather slow and that incomplete coupling took place under our reaction conditions. Equally important, some of the living ends remain intact until quenched with water.

The silyl enol ethers 1–4 were thus found to be efficient quenchers for the living cationic poly(IBVE), and in particular, those with strongly electron-donating substituents (1 and 2) are most suitable coupling agents.

The ^{13}C NMR chemical shifts [$\delta(C^\beta)$] of the enol ether carbons listed in Table I show that the enol ether β-carbon resonates at higher field in the case where the α-substituent is more electron-donating. Therefore, the β-carbon of an enol ether with a strongly electron-donating substituent is more electron-rich and thus more reactive toward the living cationic polymer, and thereby undergoes a faster quenching reaction.

Bifunctional Silyl Enol Ether Coupling Agents. On the basis of the screening discussed above, four bifunctional silyl enol ethers (5–8; Scheme III) were examined as coupling agents for the living poly(IBVE). These compounds have enol ether groups structurally similar to those in the monofunctional versions 1–4 (Scheme II).

(a) Optimization of Coupling Reaction Conditions. First, bifunctional silyl enol ether 5, bearing an electron-donating group as in the monofunctional counterpart 1, was used for coupling with the living poly(IBVE) ($\overline{DP}_n \sim 10$) in order to define the optimum reaction conditions for the chain-coupling reactions (cf. Scheme IIIA). The living poly(IBVE) was formed with the HCl/$ZnCl_2$ or HI/ZnI_2 initiating systems in CH_2Cl_2 or toluene at −15 °C ($[5]_0/[\text{living end}]_0 = {}^1/_2$). The product is a polymer (**5-P**; see below for structural verification) with a molecular weight twice that of the precursor, where two polymer chains are connected through a diketone unit derived from 5. Table II summarizes the results of these coupling reactions in which the product yield was determined by GPC on the basis of the RI-detected peak area of the coupled polymer relative to that of the starting living chain (see Figure 2 for typical examples).

Entries 1–4 of Table II show the effects of the initial $ZnCl_2$ concentration and monomer conversion on the reaction of the HCl/$ZnCl_2$-initiated living poly(IBVE) with 5 in CH_2Cl_2. When 5 was added to a reaction mixture (entry 1) at a high $ZnCl_2$ concentration and at a nearly quantitative IBVE conversion (>90%), the initially col-

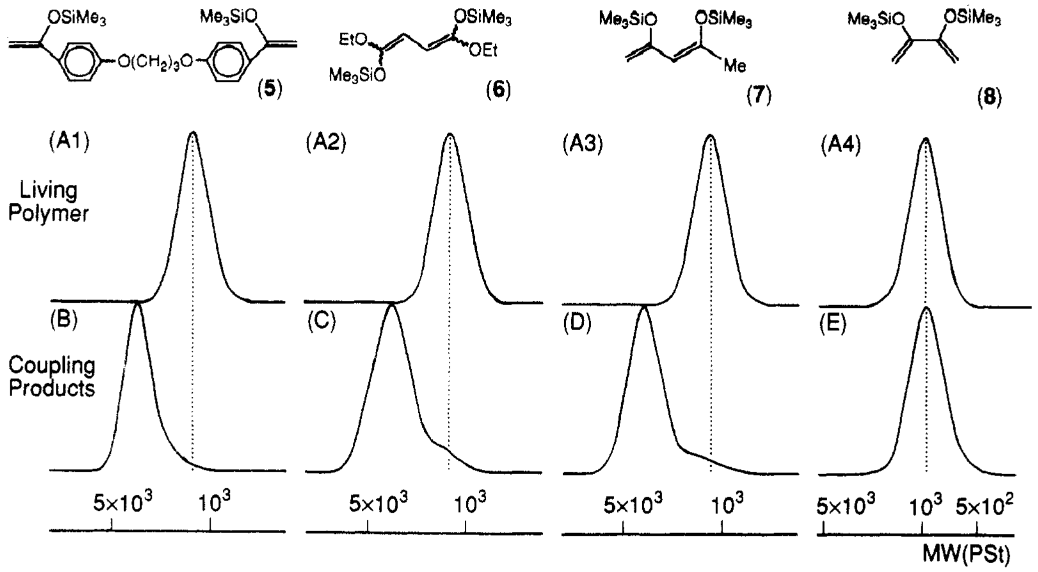


Figure 2. GPC curves of the products obtained by the coupling reactions of the HCl/$ZnCl_2$-initiated living polymer (A1–A4, quenched with methanol) with the bifunctional silyl enol ethers in CH_2Cl_2 at −15 °C for 24 h (B–D) and 4 h (E). Coupling agents: (B) **5**, (C) **6**, (D) **7**, (E) **8**. [Living polymer]$_0$ = 10 mM ($\overline{DP}_n \sim 10$); [coupling agent]$_0$ = 5 mM. Polymerization conditions are shown in footnote *a*, Table III.

Table II. Coupling Reactions of Living Poly(IBVE) with 1,3-Bis{*p*-[1-[(trimethylsilyl)oxy]vinyl]phenoxy}propane (5)

				living polymer			coupling reaction	
entry	solvent	[IBVE]$_0$, mM	[ZnX_2]$_0$, mM	time, min	conv, %	$\overline{DP}_n$[a]	time, h	yield, %[b]
			HCl/$ZnCl_2$ Initiating System					
1	CH_2Cl_2	90	1.0	6	92	9.3	5.0	88
2	CH_2Cl_2	90	0.5	15	96	9.6	24.0	87
3	CH_2Cl_2	90	0.2	35	94	9.5	24.0	88
4	CH_2Cl_2	150	0.2	15	79	12.9	24.0	>95
5	toluene	150	0.2	55	82	13.3	24.0	>95
			HI/ZnI_2 Initiating System					
6	CH_2Cl_2	100	0.1	5	96	9.6	2.0	78
7	toluene	100	0.1	10	90	9.0	6.0	83

[a] $\overline{DP}_n$ = {(conversion/100)[IBVE]$_0$ + [IBVE–HCl adduct]$_0$}/[IBVE–HCl adduct]$_0$. [b] By GPC.

orless solution turned yellow within 5 h. This coloration was absent after 24 h in the systems (entries 2 and 3) at lower $ZnCl_2$ concentrations, and the yield of **5-P** at high IBVE conversions did not exceed 90%. Some living end remained unquenched. The incomplete quenching (entries 2 and 3), as well as the yellow solution (entry 1), is apparently due to the competing deactivation of the living end, which has been suggested to occur in the near absence of the monomer.[2,10]

In contrast, when **5** was added at lower IBVE conversions (~80%) and at a low $ZnCl_2$ concentration (entry 4), a nearly quantitative coupling occurred in 24 h (Figure 2B). Almost none of the unreacted starting living polymer (cf. Figure 2A1) was detected by GPC in the product. A very similar result was obtained in the reaction carried out in toluene, a less polar solvent than CH_2Cl_2 (entry 5).

Figure 3A shows the ^1H NMR spectrum of the product obtained under the optimized quenching conditions (entry 4, Table II). The attachment of **5** to two living chains is shown by signals h–j, characteristic of the midsegment linking group derived from **5**. The intensity ratio of signal a (the terminal methyl from the initiator) to signal h (the aromatic proton of **5**) was 1.07 (theory, 1.00). In addition, the infrared spectrum of the product exhibited a carbonyl stretching band at 1670 cm^{-1}. These observations confirmed the formation of the chain-coupled polymer **5-P** (Scheme IIIA), where two living poly(IBVE) chains are connected via a diketone group derived from **5**.

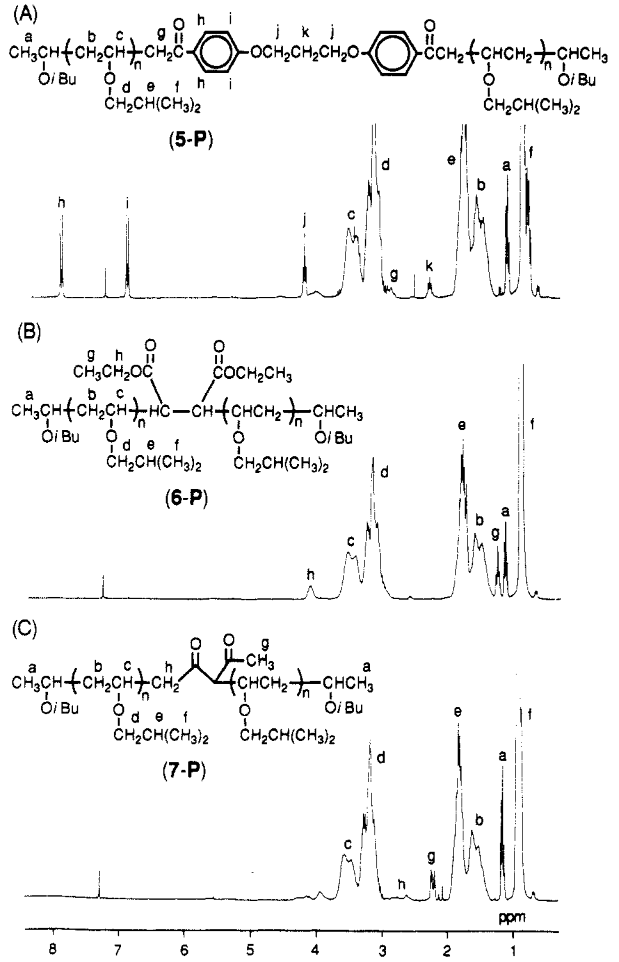


Figure 3. ^1H NMR spectra ($CDCl_3$, room temperature) of the higher molecular weight fraction separated from the respective products shown in Figure 2B–D: (A) polymer **5-P**, (B) **6-P**, (C) **7-P** (cf. Scheme III).

When similar coupling reactions with **5** were attempted for the living poly(IBVE) formed with the HI/ZnI_2 initiating system in CH_2Cl_2 and toluene (Table II, entries 6 and 7, respectively), the yields of coupled polymer **5-P**

Table III. Coupling Reactions of Living Poly(IBVE) with Bifunctional Silyl Enol Ethers[a]

		living polymer			coupling reaction	
entry	coupling agent	time, min	conv, %	$\overline{DP}_n$[b]	time, h	yield, %[c]
1	5	15	79	12.9	24	>95
2	6	10	71	11.7	24	91
3	7	10	70	11.5	24	91
4	8	10	70	11.5	4[b]	0

[a] Polymerization conditions: $[IBVE]_0$ = 150 mM; [IBVE–HCl adduct]$_0$ = 10 mM; $[ZnCl_2]_0$ = 0.2 mM; in CH_2Cl_2 at −15 °C. Coupling reaction conditions: [bifunctional coupling agent]/[living polymer]$_0$ = 1/2 in CH_2Cl_2 at −15 °C. [b] $\overline{DP}_n$ = {(conversion/100)$[IBVE]_0$ + [IBVE-HCl adduct]$_0$}/[IBVE–HCl adduct]$_0$. [b] By GPC. [d] After this short reaction period, the reaction mixture turned yellow, indicating the decay of the living end (see text; refs 2 and 10).

did not exceed 85% and were clearly lower than those with the $HCl/ZnCl_2$ initiating system, although very similar conditions were used (entries 1–3), except that the ZnI_2 concentration (0.10 mM) was low. The GPC and ^1H NMR analyses of the products showed that a part of the living ends remained unquenched and led to an aldehyde terminal during the workup (see above). Thus, in addition to the reagent concentrations and monomer conversions, the nature of the counteranion (chloride versus iodide) critically affects the coupling reaction. The better result with the chloride anion is probably due to its higher affinity toward the silicon in the enol ether[5] or to the slower deactivation of the living ends derived from $HCl/ZnCl_2$.[2c]

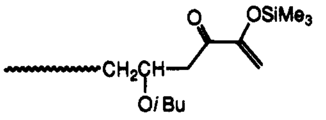
On the basis of these experiments, therefore, the following reaction conditions are concluded to be optimum for the polymer coupling with bifunctional silyl enol ether 5 (see Table II, entry 4): (i) to employ the $HCl/ZnCl_2$ initiating system; (ii) to maintain the $ZnCl_2$ (activator) concentration relatively low; and (iii) to conduct the reaction in the presence of a certain amount of monomer (conversion ~80%). These conditions have been adopted in the remaining part of this study. The polarity of the polymerization solvent does not affect the yield of the coupling, but CH_2Cl_2 was used exclusively because the reaction is faster therein.

(b) Structural Effects of Coupling Agents. Under the optimized reaction conditions (specified above), the coupling reactions were then examined by using the other bifunctional silyl enol ethers, 6–8, to compare with 5 (Scheme III). Figure 2C–E shows the GPC analysis of the products. Table III summarizes the reaction conditions and the yields of the coupled polymers (**6-P**–**8-P**) after 24-h reactions.

For 6 and 7 (entries 2 and 3, respectively), the product reached ca. 90%. Although high, this yield is slightly lower than that for 5. The major fractions of the products, separated by preparative GPC, gave the ^1H NMR spectra shown in Figure 3B,C. In spectrum B for 6, signals g and h are assigned to the carboxylate ethyl groups derived from the coupler, and the intensity ratio of signal g to signal a (the head methyl from the initiator) was 0.92 (theory 1.00). The IR spectrum of the same sample exhibited an ester carbonyl stretching band at 1732 cm^{-1}. Thus, these spectral analyses confirmed the formation of **6-P**, where two living chains are connected through the vicinal ester junction.

Similarly, the separated product from 7 (Figure 3C) showed ^1H NMR resonances g and h characteristic of the methyl and the methylene attached to the germinal ketone moiety originating from the enol ether. The intensity ratio of g to a (the head methyl) (2.03) agreed with the value (2.00) expected for polymer **7-P**. The NMR and the IR (ketone carbonyl, 1701 cm^{-1}) analyses thus verified the formation of the coupled polymer **7-P**.

By contrast, the vicinal silyl enol ether 8 turned out to be an inefficient chain-coupling agent (Table III, entry 4). While virtually no molecular weight increase was detected by GPC (Figure 2E), ^1H NMR analysis showed that the product actually consisted of a nearly 1:1 mixture of the unquenched polymer (later deactivated with water to form the aldehyde-capped form; cf. Figure 1C) and another uncoupled polymer (9) that had been formed by reaction with one of the two enol ethers with 8. As suggested for the monofunctional silyl enol ethers (Table I), the failure of polymer coupling with 9 apparently results from the lower electron density on the enol ether double bonds in 9, where each one of the electron-withdrawing silyl ethers is located α to the adjacent enol ether.



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Thus, the product yield clearly depended on the structures of the enol ether moieties of the bifunctional quenchers, increasing in the order (0% ~) 8 ≪ 7 ~ 6 ≤ 5 (~100%). As discussed above, the order primarily reflects the importance of electron-donating groups that increase the electron density in the enol ether double bond which the electrophilic (cationic) living end attacks. Although both 5 and 6 carry electron-donating α-substituents in the enol ether, the yield was higher for 5 (see Figure 2B,C). The lower efficiency with 6, small though the difference may be, is in contrast to the nearly quantitative attachment of its monofunctional counterpart 2 (Table I), and this is attributed to a steric factor specifically critical for bifunctional coupling agents. Namely, the two vicinal enol ether β-carbons in 6 are very close to each other, and once one of them reacts with a living end, the approach of a second living chain is sterically difficult.

The low yield for 7 may be due to the slow reaction (lower nucleophilicity) of its enol ethers with the living chains, as is suggested for its monofunctional model 3 (Table I). For example, when followed with time by GPC (Figure 4), the coupling reaction with 5 (traces B–D) was mostly completed within 2–6 h, whereas that with 7 (traces E–G) proceeded much more slowly (yield: 41% in 2 h and 88% in 6 h). Accordingly, the deactivation of the living end should occur during the slower coupling reaction, resulting in the lower yield of **7-P**.

(c) Effect of the Chain Length ($\overline{DP}_n$) of Living Polymers. The experiments described thus far employed short living chains with the degree of polymerization ($\overline{DP}_n$) about 10 for easy analysis of the products. As shown in Figure 5, the coupling reactions with 5–7 were also examined for longer living polymers ($\overline{DP}_n$ = 50 and 100). (See also Table IV.) Except for the difference in this variable, the reaction conditions were otherwise the same as those for the shorter chain (with the $HCl/ZnCl_2$ initiating system in CH_2Cl_2 at −15 °C for 24 h).

In the reaction with 5, which led to the nearly quantitative coupling for the short chain, the yield decreased with increasing $\overline{DP}_n$ of the living polymers (in parentheses for traces B, D, and H): >95% ($\overline{DP}_n$ = 10); 86% (50); 74% (100). Despite the decrease in yield, the products

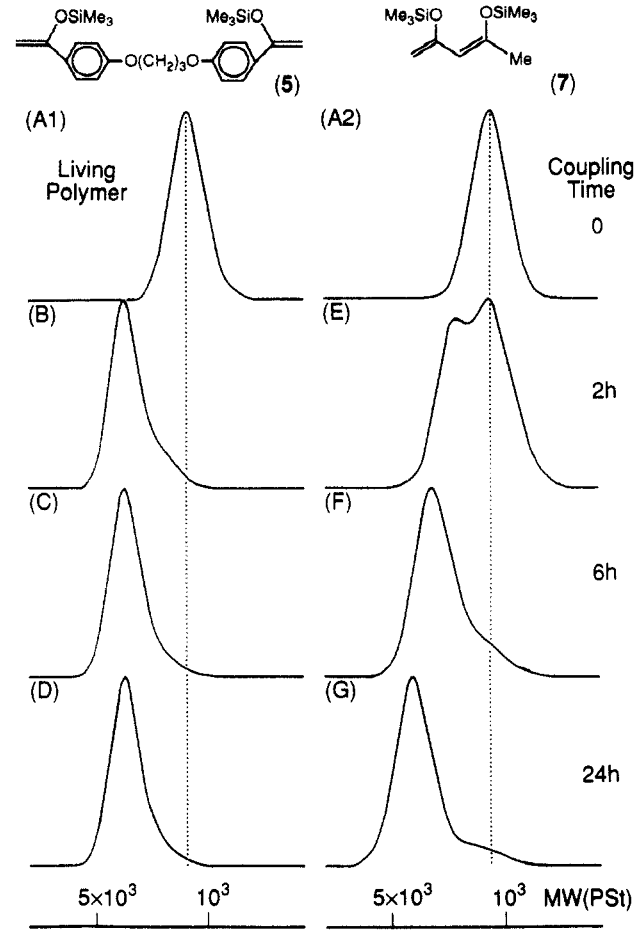

Figure 4. Reactivity of the bifunctional silyl enol ethers, **5** versus **7**. GPC curves A1 and A2 show the living polymer quenched with methanol ($\overline{DP}_n \sim 10$), and B–G the coupling products. Coupling agents: (B–D) **5**, (E–G) **7**; [coupling agent]$_0$ = 5 mM. Coupling reaction conditions: [living polymer]$_0$ = 10 mM in CH_2Cl_2 at −15 °C for 2 h (B and E), 6 h (C and F), and 24 h (D and G).

Table IV. Yields of 5-P, 6-P, and 7-P for Living Polymers of Different Chain Lengths (Cf. Figure 5)

	yield, %		
coupling agent	$\overline{DP}_n$ = 10	$\overline{DP}_n$ = 50	$\overline{DP}_n$ = 100
5	>95 (B)	86 (D)	74 (H)
6		67 (E)	64 (I)
7		73 (F)	70 (J)

were invariably the coupled polymer **5-P**. Similar trends were seen for **6** and **7**, but the coupling yields were still lower than those with **5** (traces E, F, I, and J). For example, with $\overline{DP}_n$ = 50, the coupling yield was in the order 86% (**5**) > 73% (**7**) > 67% (**6**). The particularly low yield for the longer chain with **6** further corroborates the serious steric hindrance associated with this vicinal enol ether (see section b above), where the distance between the two coupling sites (the enol ether β-carbons) is the shortest among the three coupling agents.

Conclusions. Bifunctional silyl enol ethers **5**–**7** proved efficient coupling agents for the HCl/$ZnCl_2$-initiated living poly(IBVE). The effectiveness of the silyl enol ethers, in general, originates from their high solubility in organic solvents and from the high affinity of the silicon toward the chloride counteranion of the living end. Compound **5** led to a nearly quantitative coupling reaction for relatively short living chains. The factors that favor the coupling with **5** include (i) the attachment of the electron-donating *p*-alkoxyphenyl group to the α-carbon of the enol ether double bond, which increases its electron density and hence its reactivity toward the electrophilic living end; and (ii) the favorable spatial separation of the two enol ether moieties by the long and rigid spacer, which eliminates the steric hindrance in the coupling of two polymer chains.

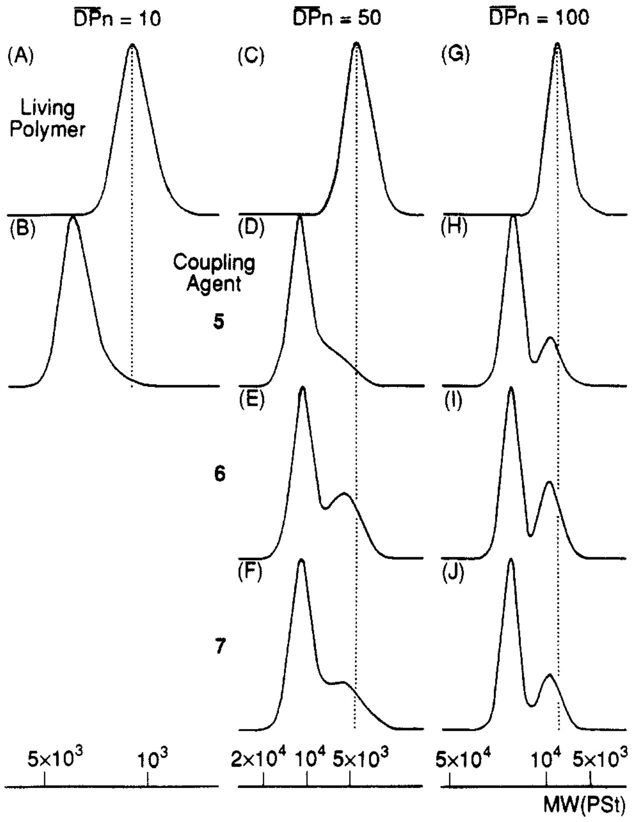

Figure 5. Effects of the chain length ($\overline{DP}_n$) of living polymers. GPC curves A, C, and G show the living polymers quenched with methanol [$\overline{DP}_n$: (A) 10; (C) 50; (G) 100]. Coupling reaction conditions: [living polymer]$_0$ = 10 mM, [coupling agent]$_0$ = 5 mM in CH_2Cl_2 at −15 °C for 24 h. The yields of **5-P**, **6-P**, and **7-P** are summarized in Table IV.

Experimental Section

Materials. (a) Polymerization Reagents. Toluene, *n*-hexane, and methylene chloride (solvents) and isobutyl vinyl ether (monomer) were washed by the usual methods[11] 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 iodide (Aldrich, purity >99.99%), used without further purification, was vacuum dried and then dissolved in the diethyl ether under dry nitrogen before use. Zinc chloride (Aldrich, 1.0 M in Et_2O) was used as received. Hydrogen iodide (dissolved in *n*-hexane) was obtained by the dehydration of commercial hydroiodic acid using phosphorus pentoxide.[11] IBVE–HCl adduct (*n*-hexane solution) was prepared as reported.[7b]

(b) Coupling Agents. Among the eight silyl enol ethers (**1**–**8**) employed, the following were purchased commercially and used as received: methyl trimethylsilyl dimethylketene acetal (**2**, Aldrich, purity 95%), 2-[(trimethylsily)oxy]propene (**3**, Shinetsu, purity 98%), 1-[(trimethylsilyl)oxy]-1-pentene (**4**, Aldrich, purity 98%), and 2,3-bis[(trimethylsilyl)oxy]-1,3-butadiene (**8**, Aldrich, purity 95%). 1,4-Diethoxy-1,4-bis[(trimethylsilyl)oxy]-1,3-butadiene (**6**, purity 99%)[10] and 2,4-bis[(trimethylsilyl)oxy]-1,3-pentadiene (**7**, purity 99%)[11] were prepared by literature methods and were identified by ^1H and ^{13}C NMR spectroscopy. Other bifunctional silyl enol ethers, **1** and **5**, were synthesized as described below.

(c) Synthesis of *p*-Methoxy-α-[(trimethylsilyl)oxy]styrene (1). The reaction was carried out under dry nitrogen in a baked 100-mL flask equipped with a three-way stopcock and a magnetic stirrer.[12] As in the other syntheses described herein, triethylamine and acetonitrile (Wako, guaranteed reagent) were purified by double distillation over calcium hydride before use, and the other reagents were employed as received from commercial sources. To a solution of *p*-methoxyacetophenone (8.4 g, 0.056 mol), sodium iodide (9.7 g, 0.065 mol), and triethylamine (9.5 mL, 0.068 mol) in acetonitrile (50 mL) was added trimethylchlorosilane (8.6 mL, 0.068 mol) dropwise at room temperature. After 1 h of stirring, the low-boiling substances such as acetonitrile were removed by evaporation under reduced pressure. The residue was diluted with dry *n*-hexane (50 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 remove the *n*-hexane, and the residue was distilled under reduced pressure and dry nitrogen to give pure 1 as a clear viscous oil [bp 98.5 °C/2 Torr; yield >95% based on *p*-methoxyacetophenone; purity >99% (^{1}H NMR)]. ^{1}H NMR ($CDCl_3$): δ 0.27 (s, $SiCH_3$), 3.80 (s, OCH_3), 4.33, 4.80 (dd, $=CH_2$), 6.85 and 7.52 (dd, C_6H_4) ppm.

(d) Synthesis of 1,3-Bis{*p*-[1-[(trimethylsilyl)oxy]vinyl]-phenoxy}propane (5). This bifunctional silyl enol ether was synthesized from 1,3-bis(4-acetylphenoxy)propane (10). In a 300-mL Erlenmeyer flask, 4-hydroxyacetophenone (10.53 g, 0.077 mol) in dimethyl sulfoxide (DMSO, 50 mL) was added dropwise to a magnetically stirred solution of potassium *tert*-butoxide (9.6 g, 0.077 mol) in the same solvent (100 mL) at room temperature. After 30 min of stirring during which the reaction mixture turned red, 1,3-dibromopropane (3.92 mL, 0.039 mol) in DMSO (50 mL) was added dropwise, and the solution was stirred for an additional 24 h at 25 °C. The mixture was then extracted three times with methylene chloride (300 mL), and the methylene chloride phase was washed three times with aqueous 5% NaOH (300 mL) and water (300 mL) and dried over anhydrous sodium sulfate overnight. The methylene chloride was removed by evaporation under reduced pressure, and the residue was twice recrystallized from a methylene chloride/methanol mixture (1/1 v/v) to give the precursor 10 as a white powdery solid (6.23 g, yield 52% from the acetophenone). ^{1}H NMR ($CDCl_3$): δ 2.32 (quintet, $-OCH_2CH_2CH_2O-$), 2.56 [s, $C(O)CH_3$], 4.22 (t, OCH_2), 6.95, 7.94 (dd, C_6H_4) ppm.

In a 100-mL, nitrogen-filled, baked flask equipped with a three-way stopcock and a magnetic stirring bar was prepared a solution of 10 (3.7 g, 0.012 mol), sodium iodide (4.8 g, 0.032 mol), and triethylamine (3.7 mL, 0.027 mol) in an acetonitrile/methylene chloride mixture (50/15 mL). Trimethylchlorosilane (3.4 mL, 0.027 mol) was added dropwise via a dry syringe at 25 °C with stirring. The mixture was stirred for 2 h and then extracted with dry *n*-hexane (50 mL). After filtration as for 1 (see above), the extract was evaporated under reduced pressure to give the bis(silyl enol ether) 5 as a yellowish oil (3.6 g, yield 66% from 10). ^{1}H NMR ($CDCl_3$): δ 0.26 (s, $SiCH_3$), 2.18 (quintet, $-OCH_2CH_2CH_2O$), 4.06 (t, OCH_2), 4.32, 4.79 (dd, $=CH_2$), 6.81, 7.50 (dd, C_6H_4) ppm. Since the acetyl groups in 10 were nearly quantitatively converted into silyl enol ethers (>99% by ^{1}H NMR), 5 was directly dissolved in methylene chloride without further purification and stored in ampules under dry nitrogen until used. The concentration of 5 was given by the population ratio obtained from the ^{1}H NMR spectrum of the mixture of 5 (0.5 mL in CH_2Cl_2) and 1,3,5-trimethoxybenzene (0.5 mL; 113.6 mM in CCl_4) with an acetone-d_6 capillary cell for external lock signal.

Procedures. (a) Polymerization and Coupling Reactions. As a representative example, the reaction of a living poly(IBVE) and the bifunctional coupling agent 5 (Table II, entry 4) is described below. 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.[1] A mixture of IBVE (0.2 mL), CCl_4 (0.2 mL, internal standard for GC analysis of IBVE), and methylene chloride (7.6 mL) was cooled to −15 °C, and solutions of 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 ($\overline{DP}_n \sim 10$; [living end] = 10 mM) was formed in near quantitative yield after 15 min. To this solution kept at −15 °C was added the methylene chloride solution of 5 (1.0 mL; $[5]_0$ = 50 mM; see above) at room temperature, quickly and with vigorous stirring. The mixture was stirred at −15 °C for an additional 24 h, subsequently washed three times with water (30 mL), evaporated to dryness under reduced pressure, and finally vacuum dried to give the coupled polymer (5-P; Scheme III). The living polymerization of IBVE with HI/ZnI_2 was carried out as reported previously.[1]

(b) Polymer Characterization. Gel permeation chromatography (GPC) 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 ($\overline{M}_n$) and the MWD of the polymers were determined by comparison to polystyrene standard samples. ^{1}H NMR spectra (270 MHz) were recorded on a JEOL GSX-270 at room temperature. IR spectra were obtained with a Shimadzu FT IR-8100 in a KBr solution cell (solvent: anhydrous carbon tetrachloride) at 25 °C.

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(8) For example, F_n = [(h + i)/4](a/3) for polymer 1-P (Figure 1A). Specifically for polymer 2-P, the α-end methyl signal a overlaps with the geminal methyl peak g of the ω-end (Figure 1B). Thus, for this polymer F_n was obtained from the intensity ratio h/(a + g − 2h).

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