Multifunctional Coupling Agents for Living Cationic Polymerization. 6. Synthesis of Multiarmed and End-Functionalized Poly(α-methylstyrene) with Multifunctional Silyl Enol Ethers

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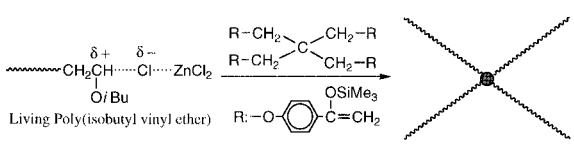
ABSTRACT: Tri- and tetraarmed polymers (**3-P** and **4-P**) of α-methylstyrene (αMeSt) and their end-functionalized versions (**12**) [$R_{4-m}C\{CH_2OC_6H_4COCH_2-(\alpha MeSt)_n-CHMeOCH_2CH_2-X\}_m$ (Me = CH_3); arm number m = 3 (R = Me), 4; X = Cl, OCOMe, OCOCMe=CH_2] have been synthesized by coupling reactions of living poly(αMeSt) with multifunctional silyl enol ethers [$R_{4-m}C\{CH_2OC_6H_4C(OSiMe_3)=CH_2\}_m$; **3**, m = 3, R = Me; **4**, m = 4]. The living poly(αMeSt) was prepared by living cationic polymerization in methylene chloride solvent at −78 °C with the hydrogen chloride−vinyl ether adduct [Cl−CHMe(OCH_2-CH_2−X)] as initiator in conjunction with tin tetrabromide ($SnBr_4$). Subsequently, the living chains were allowed to react with **3** or **4** in the presence of *N*-ethylpiperidine to give the target multiarmed polymers in high yield (>90%). Specifically for αMeSt, it proved crucial that *N*-ethylpiperidine and similar nucleophiles should be added into the living polymer solution for its efficient coupling to occur. In the end-functionalized polymers (**12**), each of the four poly(αMeSt) arms carries a terminal function X, which would provide a novel cross-linking agent [X = OH (from OCOMe)] or a tetraarmed macromonomer (X = methacryloyl).

Introduction

Coupling reactions of living polymers with multifunctional terminating agents provide methods for the synthesis of multiarmed polymers as well as telechelic and end-functionalized star polymers. In cationic polymerization, our recent systematic search has led to a certain class of silyl enol ethers that are effective in the coupling reactions of living poly(vinyl ethers) (eq 1).[2−4] According to these studies, the critical factors in these coupling processes include the following:[2,3] (i) multifunctional terminating agents should be neutral compounds well soluble in organic polymerization solvents, for which silyl enol ethers are suited; (ii) the living ends should carry the chloride counteranion, whose high affinity toward silicon facilitates efficient coupling reactions; (iii) the enolates should carry electron-donating substituents at the α-carbon of the enolate's double bond to which living ends add; and (iv) the multiple coupling sites should be attached to a rigid radial core (like the tetrasubstituted methane in eq 1) by which they are spatially well separated to avoid steric hindrance on the coupling of more than two living chains. The silyl enol ether-coupling processes shown in eq 1 turned out to fulfill all these criteria, which have, however, been tested only in vinyl ether polymerizations.



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This study[5] is to expand the scope of our coupling reactions to the living cationic polymerization of styrene derivatives that we have recently been developing.[6] Among these, we herein selected one for α-methylstyrene (αMeSt) initiated by the hydrogen chloride−vinyl ether adduct (**1**) in conjunction with tin tetrabromide ($SnBr_4$)[7,8] (Scheme 1). Although the living end thus generated carries the chloride counteranion from the initiator **1** and thereby meets criterion ii stated above, there are several points to be examined for the efficient multiple coupling reactions, and the following comprise the objectives of this study: (a) to define which silyl enol ethers are suited for the living end of αMeSt, derived from the **1**/$SnBr_4$ system, that would be less stable than those of vinyl ethers; (b) to establish optimal reaction conditions, where, as it turned out, some nucleophilic additives are in fact needed to prevent side reactions; (c) to apply the coupling processes to the synthesis of tri- and tetraarmed polymers of αMeSt, which will provide star polymers with rigid arm chains differing from the flexible counterparts based on vinyl ethers; and (d) to synthesize end-functionalized and multiarmed poly(αMeSt).

Scheme 1 illustrates the synthetic routes for these polymers based on our search (objective a), where the terminating/coupling agents are bi- to tetrafunctional silyl enol ethers (**2**−**4**) with electron-donating *p*-alkoxyaryl groups and rigid radial cores (criteria i and iv listed above). As shown for vinyl ethers, the living ends are expected to electrophilically attack the *β*-carbon of the enolate's double bond to give a ketone moiety after releasing trimethylsilyl chloride. Thus the products will be a series of multiarmed polymers (**2-P** to **4-P**).

Results and Discussion

1. Search of Coupling Agents—Model Reactions with Monofunctional Silyl Enol Ethers. The first phase of this work was concerned with the search of silyl enol ethers suited specifically for the **1**/$SnBr_4$-initiated living poly(αMeSt). For this purpose, we examined model coupling reactions with four monofunctional silyl enol ethers (**6**−**9**) (Scheme 2). The living cationic polymerization of αMeSt was carried out in methylene

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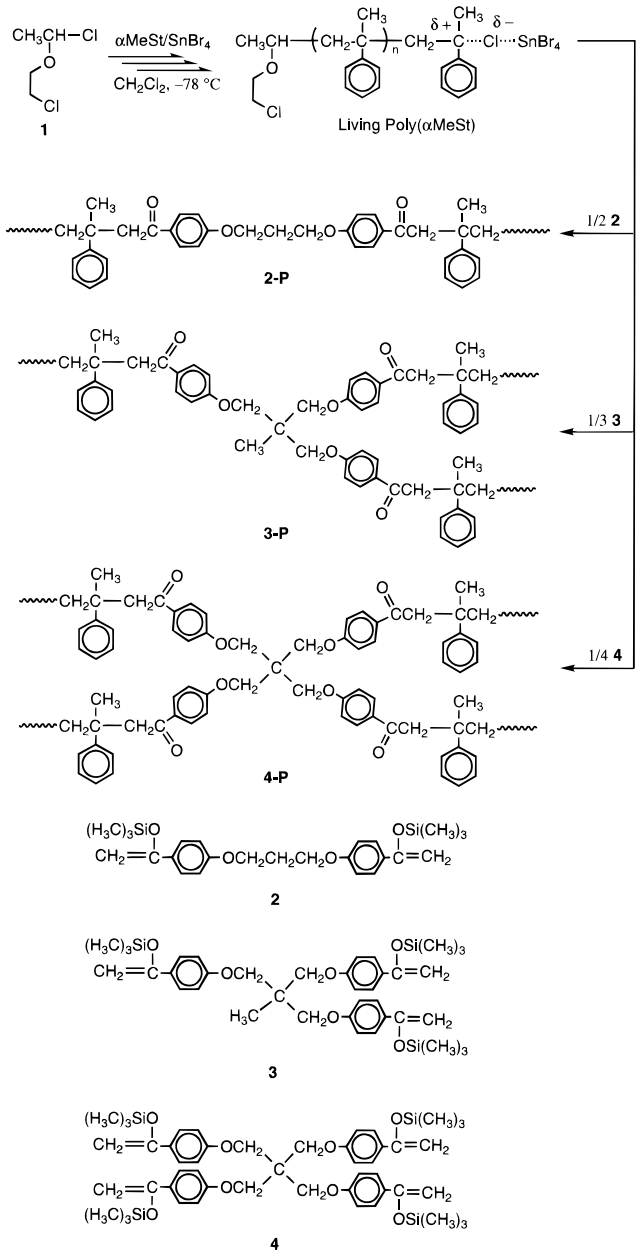
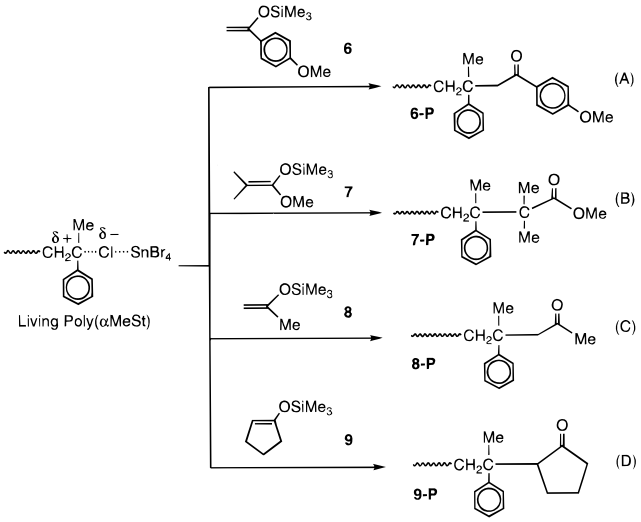
Scheme 1. Synthesis of Multiarmed Poly(α-MeSt) with Multifunctional Silyl Enol Ethers



chloride solvent at −78 °C.[7] To the solutions of the as-prepared living chains ($\overline{DP}_n$ = 20; αMeSt conversion ~ 90%), the four enolates (**6**−**9**) were separately added at concentrations slightly above that of the living ends ([coupling agent]/[living end] = 1.2) and were then allowed to react at −78 °C for 30 min. Quenching with methanol was also carried out as reference under the identical conditions. Table 1 summarizes the results and other relevant data.

After the reactions with the four silyl enol ethers, the recovered polymers invariably gave narrow molecular distributions (MWD) that are similar to those with the methanol-quenched polymers (Table 1). Figure 1 shows the ^{1}H NMR spectra of the typical products obtained with **6** and **8**, along with methanol. The $\overline{M}_n$ was determined from the peak intensity ratio of the main-chain aromatic protons (signal *g*) to the initiator residue (*b* + *f*).[7] These values are close to those by gel permeation chromatography (GPC) based on a poly(αMeSt) calibration (Table 1).

Scheme 2. Model Coupling Reactions of Living Poly(αMeSt) with Monofunctional Silyl Enol Ethers



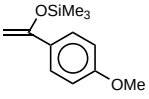
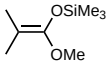
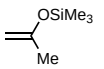
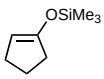
As already reported,[7] the living polymer quenched with methanol (Figure 1A) had mainly the tertiary chloride terminal (peak *e*) along with a minor amount of the exo-olefin terminal (peak *h*) due to the dehydrochlorination during workup; no signals were detectable for the methoxide group from methanol. Thus, the end-functionality ($\overline{F}_n$) for the terminal chloride reached 96% (Table 1).

In contrast, the polymer treated with **6** (Figure 1B) showed signals of neither the chloride nor the olefin, and instead those of the *p*-methoxyphenyl ketone moiety derived from the silyl enol ether (cf. Scheme 2). In particular, signals *l* (*p*-methoxy) and *j* + *k* (the aromatic protons) are clearly seen. The end-functionality based on the analysis was 0.91, indicating a nearly quantitative attachment of the silyl enol ether residue to the polymer end. The spectrum with quencher **8** (Figure 1C), on the other hand, exhibited peaks both from the enolate (e.g., signal *j*; acetoxy) and the terminal olefin (signal *h*). Peak integration indicated that only 31% of the polymer terminal carries the expected ketone group (Table 1, entry 3). Similar results were obtained with the other two enol ethers, **7** and **9** (Table 1, entries 2 and 4).

Thus, as with vinyl ethers,[2] the aromatic silyl enol ether **6** is the best terminating agent among the four for the living poly(αMeSt).[9] Inspection of the ^{13}C NMR chemical shifts of the enol ether double bonds (C^{β}) shows that this compound has the highest electron density on the β-carbon where the growing carbocation reacts, and the importance of an electron-donating substituent on the enol ether carbon has also demonstrated for αMeSt.

2. Coupling Reactions with Multifunctional Silyl Enol Ethers. (a) Optimization of Coupling Reactions. On the basis of these model reactions and search of the best coupling moieties, we thus decided to employ the multifunctional versions of **6** (compounds **2**−**4**; Scheme 1) that carry silyl enol ether groups almost identical to that in **6** along with a rigid and radial core. The first set of experiments were carried out under similar conditions as with the monofunctional agents, and **2**−**4** were added to solutions of the living poly(αMeSt) at conversions ca. 90%. Because of the multiple nature of the terminating functions, their mole ratios to the living ends were strictly stoichiometric; i.e., [living end]/[coupling agent] = 2, 3, and 4 for **2**, **3**, and **4**, respectively.[10]

Table 1. Model Coupling Reactions of Silyl Enol Ethers with Living Polymer[a]

entry	coupling agent	$\delta(C^{\beta})^b$ (ppm)	$\delta(C^{\alpha})^b$ (ppm)	$\overline{M}_n \times 10^{-3}$ (^{1}H NMR)	$\overline{M}_n \times 10^{-3}$ (GPC)[d]	$\overline{M}_w/\overline{M}_n$ (GPC)	$\overline{F}_n$[e] (^{1}H NMR)
	MeOH			3.1	2.5	1.14	0.96[f]
1	 **6**	89.3	155.3	3.4	2.6	1.15	0.91
2	 **7**	90.6	149.3	2.7	2.2	1.18	0.29
3	 **8**	91.2	155.9	2.9	2.5	1.15	0.31
4	 **9**	101.9	154.9	2.8	2.6	1.18	0.21

[a] Coupling reaction conditions: [coupling agent]/[living polymer] = 1.2; in CH_2Cl_2 at −78 °C for 30 min. Polymerization conditions: [αMeSt]$_0$ = 150 mM; [initiator **1**]$_0$ = 10 mM; [$SnBr_4$]$_0$ = 20 mM; in CH_2Cl_2 at −78 °C for 2 min; conversion ∼ 90%. [b] ^{13}C NMR chemical shifts of the α- and β-carbons of silyl enol ether: C^{β}═C^{α}—$OSiMe_3$. [c] $\overline{M}_n$(^{1}H NMR) = $\overline{DP}_n$(^{1}H NMR) × (mol wt of αMeSt) + (formula wt of the initiator and the ω-end group), $\overline{DP}_n$(^{1}H NMR) was determined from the peak areas of the α-end group and main chain aromatic protons. [d] $\overline{M}_n$(GPC) was determined on the basis of a poly(αMeSt) calibration. [e] $\overline{F}_n$ = (ω-end group)/(α-end methyl group), by ^{1}H NMR. [f] For the carbon−chloride bond terminal group derived from methanol quenching.

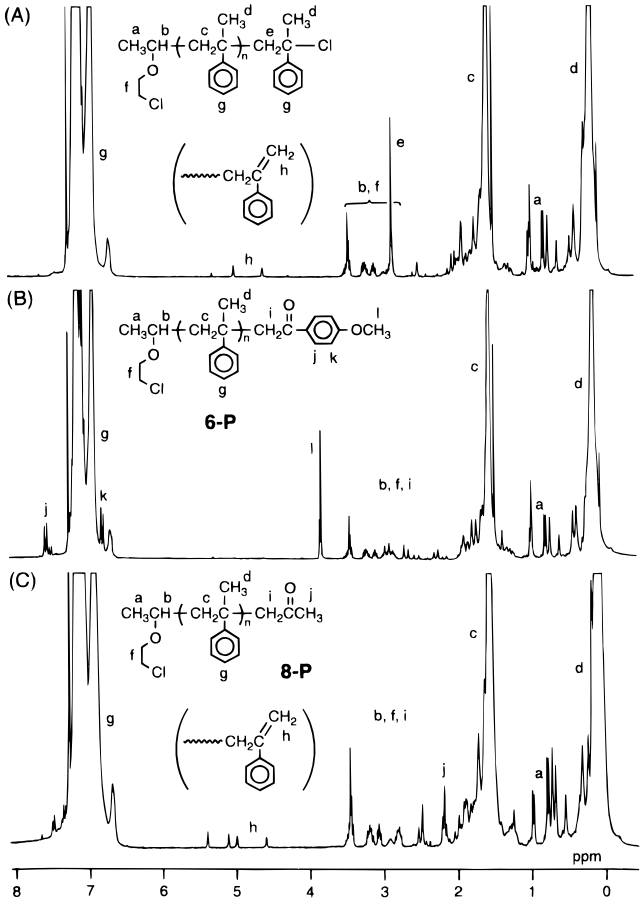


Figure 1. ^{1}H NMR spectra of the products in the model coupling reactions of the **1**/$SnBr_4$-initiated living poly(αMeSt) with monofunctional silyl enol ethers (Scheme 2). Quenching agent: (A) methanol; (B) **6**; (C) **8**. See footnote *a* in Table 1 for reaction conditions.

The quenching reactions indeed led to products with relatively narrow, unimodal MWDs ($\overline{M}_w/\overline{M}_n$ = 1.2−1.25; Figure 2A−D), and their molecular weights increased in accordance with increasing functionality (the numbers of silyl enol ethers per molecule). However,

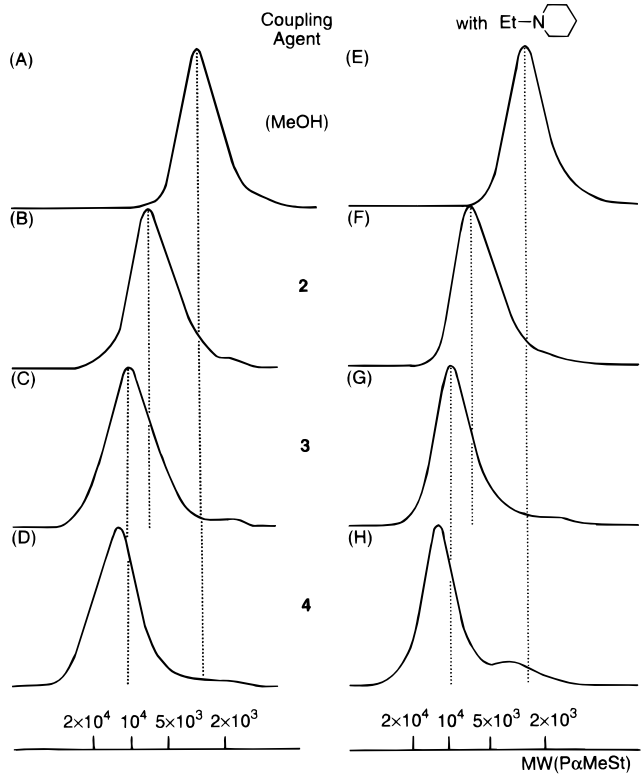


Figure 2. MWD of the products in the coupling reactions of the **1**/$SnBr_4$-initiated living poly(αMeSt) ($\overline{DP}_n$ ∼ 20) with multifunctional silyl enol ethers in the absence (A−D) and presence (E−H) of *N*-ethylpiperidine (Scheme 1). Coupling agent: (A, E) methanol (uncoupled living polymer); (B, F) **2**; (C, G) **3**; (D, H) **4**. See footnote *a* in Table 2 for the polymerization conditions. Coupling reaction conditions: in CH_2Cl_2 solvent at −78 °C; for samples B−D, [initiator **1**] = [**2**]/2 (B) = [**3**]/3 (C) = [**4**]/4 (D), for 24 h; for samples F−H, [initiator **1**] × 0.73 (initiator efficiency) = [**2**]/2 (F) = [**3**]/3 (G) = [**4**]/4 (H), for 6 h.

^{1}H NMR analysis showed that the number of the aromatic rings from the quencher per polymer chain (or the initiator residue) were larger than expected from the multiarmed structures (**2-P** to **4-P**, Scheme 2) where

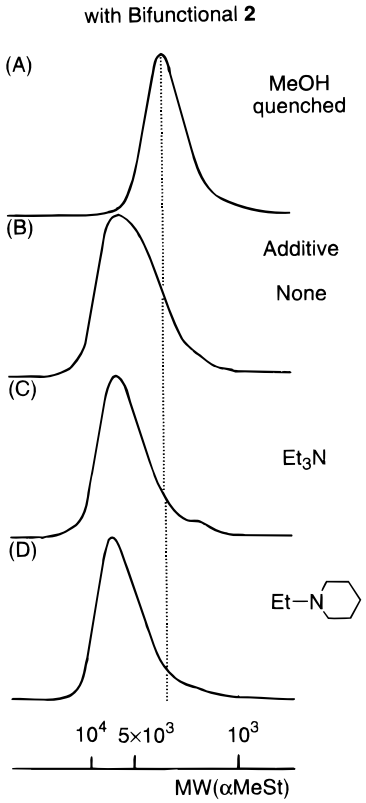


Figure 3. Effects of amine additives in the coupling reactions of the **1**/$SnBr_4$-initiated living poly(αMeSt) ($\overline{DP}_n \sim 20$) with **2**. Coupling agent/additive: (A) methanol, none (uncoupled polymer); (B) **2**, none; (C) **2**, triethylamine; (D) **2**, *N*-ethylpiperidine. See footnote *a* in Table 2 for reaction conditions.

each arm chain is connected to one aromatic spacer ring; namely (aromatic ring per chain): **2**, 1.64; **3**, 1.35; **4**, 1.32; theory, 1.00. On the basis of NMR analysis, we concluded that the living poly(αMeSt) end reacts with the silyl enol ether more slowly than the vinyl ether counterpart and that, during the slow quenching process, the unreacted double bonds of the enol ether might undergo cationic oligomerization to form an oligomeric core. Note that the double bond is a derivative of the highly reactive α-substituted silyl vinyl ether prone to cationic polymerization.

(b) Effects of *N*-Ethylpiperidine and Related Nucleophiles. The coupling process between a silyl enol ether [CH_2=CR($OSiMe_3$)] and a living cationic polymer (~~C^+) consists of the attack of the cation toward the enol ether double bond and the subsequent release of the trimethylsilyl group (as Me_3SiCl) from the resultant silyloxy carbocation:[2,3]

$$\sim\sim C^+ + CH_2{=}CR(OSiMe_3) \rightarrow \sim\sim C{-}CH_2C^+R(OSiMe_3) \rightarrow \sim\sim C{-}CH_2CR{=}O$$

We estimated that the primary reason for the slow quenching would be that the release of the trimethylsilyl group was slow, particularly at −78 °C. Thus, we examined the possibility of accelerating this process by adding nucleophiles that are known to coordinate the silyl moiety and facilitate its cleavage from the enol ether oxygen in the aldol and related reactions.[11,12]

Figure 3 shows the effects of amines on the MWDs of poly(αMeSt) quenched with the bifunctional coupling agent **2**. The additives were added immediately after the addition of **2** into the living polymer solution ($\overline{DP}_n = 20$; conversion ~ 90%; [amine] = [initiator **1**]). The product for the quenching without additive (Figure 3B) shows a MWD that apparently comprises two fractions, one for the coupled polymers with molecular weights doubled from the precursor, and the other for the dead precursor (cf. Figure 3A for the methanol-quenched living polymer). The comparison again indicates that, without any additive, the polymer coupling (quenching) is slow, during which a part of the remaining living end probably decayed.

On the other hand, the quenching in the presence of triethylamine and *N*-ethylpiperidine[13] (Figure 3, C and D, respectively) led to products with clearly narrower MWDs and doubled molecular weights relative to the precursor (Figure 3A); no appreciable tailing due to dead, uncoupled chains is seen. As will be shown later, in particular, *N*-ethylpiperidine proved well suited for enhancing the coupling reactions with **2** (and its higher analogs **3** and **4**) and gives chain-coupled polymers where quencher **2** combines two living chains without side reactions (i.e., one aromatic ring per chain, by ^1H NMR). Rather unexpectedly, other nucleophiles often employed in the organic reactions of silyl enol ethers, such as the bifluoride[14] and benzoate[15] anions, did not improve the coupling reactions under similar conditions.

Thus, the quenching reactions of the living poly(αMeSt) with multifunctional silyl enol ethers require the presence of nucleophiles, *N*-ethylpiperidine in particular, for clean and quantitative polymer coupling. It should be noted that such additives are needed neither for the corresponding reaction with the monofunctional silyl enol ethers (**5**−**9**; see above) nor for the coupling of living poly(vinyl ethers) even with multifunctional reagents.[2,3]

3. Synthesis of Bi- to Tetraarmed Polymers. Based on the encouraging results with *N*-ethylpiperidine, the coupling reactions with the three multifunctional silyl enol ethers were reexamined (Figure 2E−H). When the living poly(αMeSt) ($\overline{DP}_n \sim 20$) and **2**−**4** were allowed to react in the presence of the cyclic amine for 6 h at −78 °C, all the products gave sharp, unimodal MWDs with clearly increased molecular weights in accordance with the increasing functionality of the silyl enol ethers. In Figure 2, comparison between the product MWDs with and without the piperidine, or traces B−D (the left column) versus F−H (the right column), shows appreciable improvements by the additive. The apparent yields of the coupling products are close to quantitative for di- and trifunctional quenchers, whereas it was around 90% with the tetrafunctional counterpart. The slightly low yield for the last would result from the steric hindrance upon coupling of four poly(αMeSt) chains, whose α-methyl groups render them bulkier and more rigid than poly(vinyl ethers).

These coupled products were fractionated by preparative GPC and subjected to structural analysis by ^1H NMR spectroscopy (Figure 4 and Table 2). The spectra for the three quenchers are consistent with the structures for **2-P** to **4-P** (Scheme 1), showing, for example, signals due to the methylene (*a*) and aromatic protons (*b* and *c*) of the core and the α-end methyl (*h*) from the initiator **1**, along with the poly(αMeSt) main chains. The integrated peak areas of the α-end methyl relative to the core methylene protons (ratio *h*/*a*) gave the number of the core aromatic ring per arm chain (Table 2), which are all close to unity as expected from the quantitative coupling reactions. Note that these values for the reactions without the piperidine additive were larger

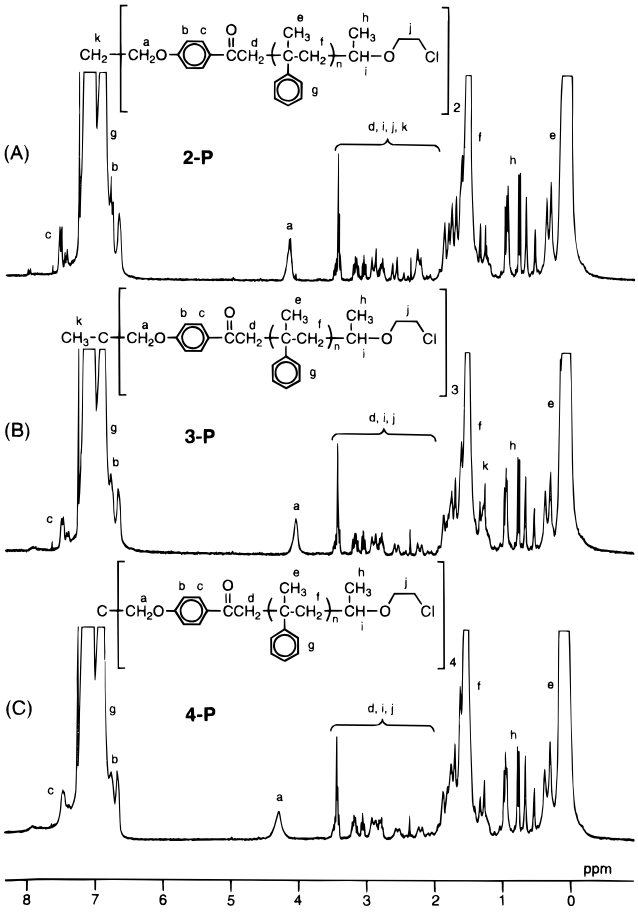
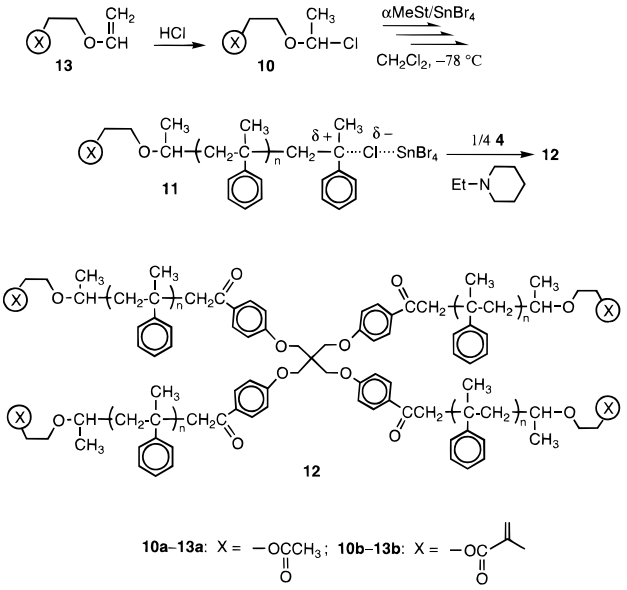


Figure 4. ^{1}H NMR spectra of the products (samples F−H, Figure 2) in the coupling reactions of the **1**/$SnBr_4$-initiated living poly(αMeSt) with multifunctional silyl enol ethers (Scheme 1). Coupling agent: (A) **2**; (B) **3**; (C) **4**. See footnote *a* in Table 2 for reaction conditions.

than unity (see above). The $\overline{M}_n$'s of the coupling products (both by NMR and GPC; Table 2) increase in accordance with the functionality of the coupling agents, while the arm molecular weights are nearly constant (∼22).

Thus, the coupling reactions of the **1**/$SnBr_4$-initiated living poly(αMeSt) with silyl enol ethers **2**−**4** led to well-defined di- to tetraarmed polymers in high yields. As emphasized already, the keys to the efficient coupling reactions are the selection of suitable silyl enolate coupling agents and, specifically for poly(αMeSt), the use of *N*-ethylpiperidine as a nucleophilic additive that enhances the reactivity of the silyl enol ether moiety.

Scheme 3. Synthesis of End-Functionalized Tetraarmed Poly(αMeSt) with Tetrafunctional Silyl Enol Ether 4



4. Synthesis of End-Functionalized Multiarmed Polymers. An immediate extension of our coupling reactions is the synthesis of end-functionalized poly(αMeSt), as illustrated in Scheme 3, where the living chain to be coupled bears an α-end functional group. We have already reported that such end-functionalization is feasible for αMeSt also by replacing the initiator (**1**; Scheme 1) with functionalized versions (**10**).[8] As does **1**, these initiators induce living αMeSt polymerization in the presence of $SnBr_4$ to give end-functionalized linear polymers (**11**). They may subsequently be coupled with the tetrafunctional coupling agent (**4**) and others, in the presence of *N*-ethylpiperidine additive, into multiarmed polymers (**12**) in which each arm carries a terminal functional group (X) derived from the initiator **10**; X may include acetoxy (**10a**; protected hydroxy) and methacryloyl (**10b**; for macromonomers). The functionalized initiators **10** are readily prepared from the corresponding vinyl ethers (**13**) by electrophilic addition reactions with hydrogen chloride.[8]

With the two functional initiating systems, **10a** and **10b** plus $SnBr_4$, αMeSt was polymerized in methylene chloride solvent at −78 °C. A part of the resulting polymers was quenched with methanol at conversion ∼90% to confirm that they are end-functionalized living polymers with narrow MWDs (Figure 5, A1 and A2).[8] NMR analysis also confirmed their expected structures

Table 2. Coupling Reactions of Living Poly(αMeSt) with Bi-, Tri-, and Tetrafunctional Silyl Enol Ethers (2−4) in the Presence of *N*-Ethylpiperidine

entry[a]	coupling agent	$\overline{F}_n$[b] (^{1}H NMR)	$\overline{N}$(arm)[c]	% yield (GPC)	$\overline{DP}_n$(arm) (^{1}H NMR)[d]	$\overline{M}_n \times 10^{-3}$ (^{1}H NMR)	$\overline{M}_n \times 10^{-3}$ (GPC)[f]	$\overline{M}_w/\overline{M}_n$ (GPC)
1	(MeOH)	1.00	1.00	∼100	18.4[g]		2.3	1.15
2	**2**	1.03	2.06	>95	22.3	5.9	5.4	1.16
3	**3**	0.97	2.91	>95	21.6	7.9	7.9	1.19
4	**4**	0.96	3.84	89	22.6	10.8	11.3	1.16

[a] Polymerization conditions: [αMeSt]$_0$ = 150 mM; [initiator **1**]$_0$ = 10 mM; [$SnBr_4$]$_0$ = 20 mM; in CH_2Cl_2 at −78 °C for 2 min; conversion ∼ 90%; $\overline{DP}_n$(calcd) = 13.7. Coupling reaction conditions: [initiator **1**] × 0.73 (initiator efficiency) = [**2**]/2, [**3**]/3, and [**4**]/4; in CH_2Cl_2 at −78 °C for 6 h in the presence of *N*-ethylpiperidine ([*N*-ethylpiperidine] = [**5**]). [b] $\overline{F}_n$ = (α-end CH_3)/(the phenyl groups), by ^{1}H NMR; $\overline{F}_n$(theory) = 1.00. [c] The number of arms per polymer: $\overline{N}$(arm) = $\overline{F}_n$ × (the number of silyl enol ethers per coupling agent). [d] $\overline{DP}_n$ shows the degree of polymerization of the arm polymer by ^{1}H NMR. [e] $\overline{M}_n$(^{1}H NMR) = $\overline{DP}_n$(^{1}H NMR) × (mol wt of αMeSt) + (mol wt of initiator **1**) + (mol wt of ω-end group). [f] $\overline{M}_n$(GPC) was determined on the basis of a poly(αMeSt) calibration. [g] $\overline{DP}_n$ was calculated from $\overline{M}_n$(GPC): $\overline{DP}_n$ = [$\overline{M}_n$(GPC) − (mol wt of **1**)]/(mol wt of αMeSt).

Table 3. Synthesis of End-Functionalized Polymers with Tetrafunctional Silyl Enol Ethers (4) (Scheme 3)

entry[a]	coupling agent	product	end functional group	$\bar{F}_n$[d] (^{1}H NMR)	% yield (GPC)	$\bar{M}_n \times 10^{-4}$ (^{1}H NMR)[e]	$\bar{M}_n \times 10^{-4}$ (GPC)[f]	$\bar{M}_w/\bar{M}_n$ (GPC)
1	(MeOH)	**11a**	acetoxy	1.03	~100	0.37	0.27	1.12
2[b,c]	**4**	**12a**	acetoxy	3.64	89	1.4	1.3	1.11
3	(MeOH)	**11b**	methacryloyl	1.16	~100	0.24	0.25	1.14
4[b,c]	**4**	**12b**	methacryloyl	3.72	89	1.3	1.5	1.14

[a] Polymerization conditions: $[\alpha MeSt]_0 = 150$ mM; $[\mathbf{10}]_0 = 10$ mM; $[SnBr_4]_0 = 20$ mM; in CH_2Cl_2 at −78 °C; for 5 min, conversion ~ 92% (for **10a**: entries 1 and 2); for 10 min, conversion ~ 95% (for **10b**: entries 3 and 4). [b] Coupling reaction conditions: [**10a**] × 0.64 (initiator efficiency) = [**4**]/4 (entry 2); [**10b**] × 0.72 (initiator efficiency) = [**4**]/4 (entry 4); in CH_2Cl_2 at −78 °C for 6 h in the presence of *N*-ethylpiperidine ([*N*-ethylpiperidine] = [**10**]). [c] For the samples fractionated by preparative GPC from the products shown in Figure 5. [d] The number of end functional groups per polymer: $\bar{F}_n$ = (α-end CH_3)/(coupling agent moiety), by ^{1}H NMR. [e] $\bar{M}_n$(^{1}H NMR) = [$\overline{DP}_n$(^{1}H NMR) × (mol wt of αMeSt) + (mol wt of **10**)] × $\bar{F}_n$(^{1}H NMR) + (mol wt of ω-end group). [f] $\bar{M}_n$(GPC) was determined on the basis of a poly(αMeSt) calibration.

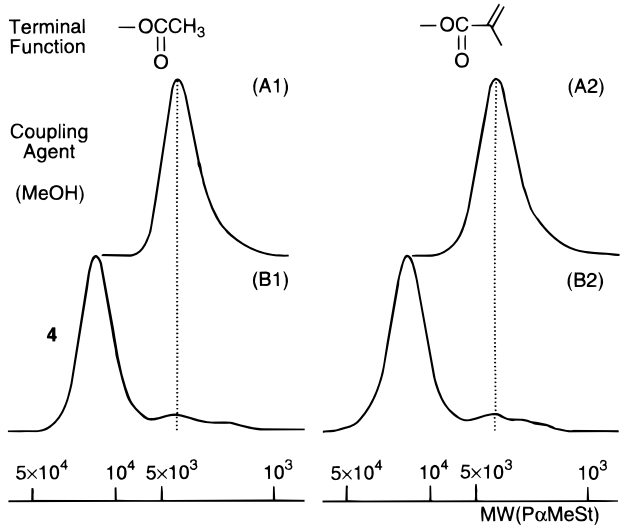


Figure 5. MWD of the products in the coupling reactions of end-functionalized living poly(αMeSt) **11** (the **10**/$SnBr_4$ system) with tetrafunctional silyl enol ether **4** in the presence of *N*-ethylpiperidine (Scheme 3). Initiator/end functional group: (A1, B1) **10a**, acetoxy; (A2, B2) **10b**, methacryloyl. Coupling agent: (A1, A2) methanol (uncoupled living polymer); (B1, B2) **4**. See footnote *a* in Table 3 for reaction conditions.

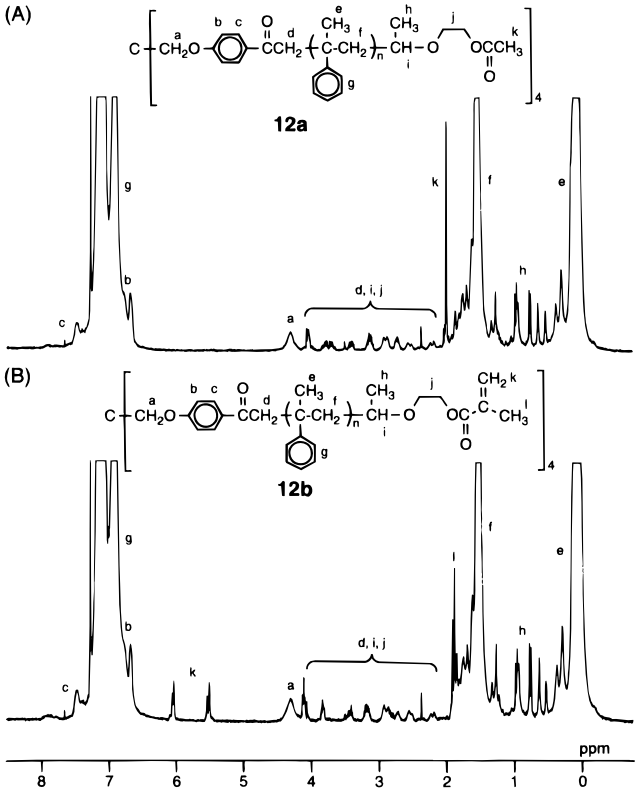


Figure 6. ^{1}H NMR spectra of the products (samples B1 and B2, Figure 5) in the coupling reactions of end-functionalized living poly(αMeSt) **11** with **4** (Scheme 3). See footnote *a* in Table 3 for reaction conditions.

where each chain has nearly one α-end functional group X (Table 3, entries 1 and 3).

The unquenched parts of the living polymers were then allowed to react with the tetrafunctional enol ether **4** in the presence of *N*-ethylpiperidine. The products exhibited narrow, unimodal MWDs (Figure 5, B1 and B2) with clearly increased molecular weights. The small fractions in the low molecular weight region are most likely the oligomers with two to three αMeSt units and indan terminals formed at the early stages of the polymerization.[7,8] From the GPC traces, the coupling yield is around 90% (Table 3).

The fractionated main products gave the ^{1}H NMR spectra shown in Figure 6, which conformed to the structures for end-fucntionalized tetraarmed polymers **12a** and **12b** (Scheme 3). In addition to the signals of the core moiety (*a*−*c*) and the poly(αMeSt) main chain (*e*−*g*), the spectra now consist of resonances from the terminal groups, such as the α-end methyl (*h*), the acetoxy (*k*, Figure 6A), and the methacryloyl (*k* and *l*, Figure 6B) protons. Integration of these signals (Table 3) also showed that each arm has nearly one terminal function ($\bar{F}_n \sim 1$) and that polymer molecular weights are nearly 4 times larger than that of the linear precursor.

Thus, despite the polar end-functional groups, the coupling reactions between the living polymer **11** and silyl enol ether **4** led to tetraarmed poly(αMeSt) (**12**) with four arm-terminal functions attached to relatively rigid and glassy, styrenic arm chains that would contrast with the previously obtained poly(vinyl ether) counterparts.[4] With its acetoxy groups, **12a** will be converted into tetrafunctional polymer alcohol that would be a new cross-linking agent, whereas with its methacryloyl groups, **12b** will be a novel tetrafunctional macromonomer.

Experimental Section

Materials. (a) Polymerization Reagents. Commercial αMeSt monomer (Wako Chemicals; purity > 98%) was washed with 10% aqueous sodium hydroxide solution and then with water, dried overnight with anhydrous sodium sulfate, and distilled twice over calcium hydride. $SnBr_4$ was obtained commercially (Aldrich; 1.0 M in CH_2Cl_2 under nitrogen) and used after dilution with dry CH_2Cl_2 at a given concentration. The initiators [$CH_3CHCl(OCH_2CH_2X)$; X = Cl (**1**), $OCOCH_3$ (**10a**), and $OCOC(CH_3)=CH_2$ (**10b**)] were prepared by bubbling dry hydrogen chloride gas into 1.0 M solutions of the corre-

sponding vinyl ethers [**13**; CH_2═CH(OCH_2CH_2X)] in *n*-hexane at 0 °C.[4,8] Methylene chloride and *n*-hexane (solvents) and tetralin (1,2,3,4-tetrahydronaphthalene; GC standard) of commercial sources were purified by the usual methods,[7,8] dried overnight with calcium base, and distilled twice over calcium hydride into stopcocked flasks containing 3 Å molecular sieves.

(b) Coupling Agents and Additives. The monofunctional (**6**−**9**)[2] and multifunctional (**2**−**4**)[3] silyl enol ethers were synthesized as reported. The concentrations of their stock solutions were determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard.[2,3] *N*-ethylpiperidine and triethylamine (Aldrich) were dried with 3 Å molecular sieves and distilled twice over calcium hydride before use. Tris(dimethylamino)sulfonium trimethylsilylbifluoride (Aldrich) and tetra-*n*-butylammonium fluoride (Tokyo Kasei; purity >98%) were used as received. Tetra-*n*-butylammonium benzoate was prepared by the literature method.[16]

Procedures. (a) Living Polymerizations and Coupling Reactions. All manipulations were carried out under dry nitrogen by the syringe technique in a 50-mL baked flask equipped with a three-way stopcock and a Teflon-coated magnetic stirring bar. A typical example is as follows: To a cooled mixture of αMeSt (0.20 mL), tetralin (0.2 mL), and methylene chloride (7.6 mL) at −78 °C were added solutions of the initiator (**1** or **10**; 1.0 mL; 0.10 M in *n*-hexane) and $SnBr_4$ (1.0 mL; 0.20 M in CH_2Cl_2) in this order with stirring. Within 2 min, conversion reached 90% or above to give living poly(αMeSt); the polymerization solutions were colorless and transparent throughout. A part of the polymers was quenched with prechilled methanol for structural and molecular weight analyses. The reagent concentrations and other details are given in Tables 2 and 3 for each experiment.

To the remaining living polymer solutions (10 mL), kept unquenched and at −78 °C, was quickly added the CH_2Cl_2 solution of the coupling agent (**2**−**4**; **2**, 0.73 mL at 50.0 mM; **3**, 0.43 mL at 56.1 M; **4**, 0.44 mL at 41.4 mM) with vigorous stirring, and, immediately after this addition, a solution of *N*-ethylpiperidine (1.0 mL; 100 mM in CH_2Cl_2) was added. Under these conditions, the mole ratio of the living end to the silyl enol ether groups in the quencher was exactly unity.[10] The mixtures were stirred at the same temperature for 6 h, washed three times with 2% hydrochloric acid (30 mL each) and subsequently three times with deionized water (30 mL each), evaporated to dryness under reduced pressure, and finally vacuum dried to give the products. The samples were subjected to GPC analysis; a part of the products for ^{1}H NMR analysis was fractionated by preparative GPC (Shodex K-2003; exclusion limit = 7×10^4; 25 mm i.d. × 30 cm).

The model coupling reactions of the living poly(αMeSt), prepared as specified above, with the monofunctional silyl enol ethers (**6**−**9**) were performed similarly, except that the quencher/living end mole ratio was 1.2.

(b) Polymer Characterization. Gel permeation chromatography (GPC) was carried out in chloroform eluent at room temperature on a Jasco Trirotar-II chromatograph equipped with three polystyrene gel columns (Shodex K-802, K-803, and K-804 in series; exclusion limit = 4×10^5; 8.0 mm i.d. × 30 cm each) and refractive index/ultraviolet dual-mode detectors. The number-average molecular weights ($\overline{M}_n$) and the MWD of the polymers were determined on the basis of a poly(αMeSt) calibration constructed with 10 standard samples (Polymer Laboratories; $\overline{M}_n$ = 3500−773000; $\overline{M}_w/\overline{M}_n$ = 1.03−1.08) as well as αMeSt dimer and trimer.[7] ^{1}H NMR spectra (270 MHz) were recorded on a JEOL GSX-270 spectrometer in $CDCl_3$ at 25 °C.

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(9) Preliminary experiments[5] also showed that similar quenching reactions fail to work on the living polymers of styrene and *p*-methylstyrene in methylene chloride at −15 °C; initiators: styrene, 1-phenylethyl chloride; *p*-methylstyrene, **1**; both in conjunction with $SnCl_4$ and nBu_4NCl. The terminal groups were invariably the chloride, even after the treatment with **6**−**9** for 30 min.

(10) Our previous[7] work indicated that the $\overline{M}_n$ of the poly(αMeSt) with the **1**/$SnBr_4$ system is higher than the value calculated from the monomer/initiator feed ratio. Although the initiator completely disappears during the early stage of the polymerization, the apparently low initiation efficiency is due to the fact that a part of the resultant initiating species does not grow into living polymers but undergoes an intramolecular cyclization (indan-ring formation), primarily at the dimer and trimer stages. Therefore, the living end concentration was empirically estimated from the ^{1}H NMR-based $\overline{M}_n$ and set 73% of the nominal initiator concentration specifically for the polymerization conditions employed throughout this work.

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