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End-Functionalized Polymers of *p*-Alkoxystyrenes by Living Cationic Polymerization. 1. *p*-Methoxystyrene

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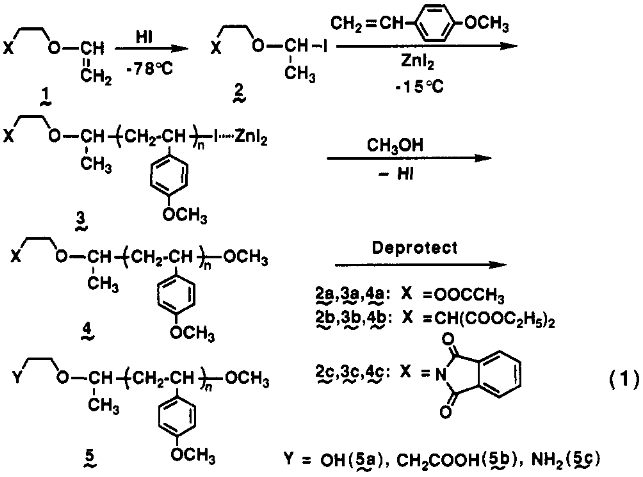
ABSTRACT: A series of end-functionalized polymers [$X—CH_2CH_2OCH(CH_3)(pMOS)_nOCH_3$ (4) (X = CH_3COO (**4a**); $(EtOCO)_2CH$ (**4b**); phthalimide (**4c**)); $H(pMOS)_nOCH_2CH_2—Z$ (**8**) (Z = $OCOCH_3$ (**8a**); $OCOC(CH_3)═CH_2$ (**8b**); $OCOCH═CH_2$ (**8c**)); and $(EtOCO)_2CHCH_2CH_2OCH(CH_3)(pMOS)_nOCH_2CH_2OCOC(CH_3)═CH_2$ (**9**)] of *p*-methoxystyrene (pMOS) were synthesized by two methods based on living cationic polymerizations with hydrogen iodide based initiating systems in toluene at −15 °C: (1) (functional initiator method) living polymerization initiated with a functional vinyl ether–hydrogen iodide adduct [$X—CH_2CH_2OCH(CH_3)I$] in conjunction with ZnI_2 to give α-end functional polymer **4**; and (2) (end-capping method) quenching the HI/ZnI_2-initiated living pMOS with a functional alcohol ($HOCH_2CH_2Z$) to give the ω-end functional polymer **8**. Combination of the two methods gave heterotelechelic poly(pMOS); e.g., **9** with a malonate and a methacrylate terminals. ^1H NMR analysis showed all these polymers to possess controlled molecular weights ($\overline{DP}_n = [pMOS]_0/[initiator]_0$), very narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n < 1.1$), and end-functionalities close to 1 or 2. The end groups of polymers **4a–c** and **8a** can be converted into hydroxy (**4a** and **8a**), carboxy (**4b**), and amino (**4c**) functions, whereas polymers **8b**, **8c**, and **9** are new (meth)acrylate-type macromonomers with a rigid poly(pMOS) chain.

Introduction

Living polymerization has been among the most effective methods for the controlled synthesis of end-functionalized polymers and oligomers, which are versatile precursors for elastomers, compatibilizers, and other advanced polymeric materials. In living cationic polymerization of vinyl monomers, the hitherto prepared end-functional polymers[2] are of flexible backbones primarily derived from vinyl ethers[3–11] and isobutylene.[12,13] Few have been known for their counterparts of rigid backbones, particularly those from styrene derivatives, in marked contrast to the ample examples that have been obtained by living anionic polymerization.[14]

Recently, we have achieved living cationic polymerizations of *p*-methoxystyrene (pMOS)[15] and *p-tert*-butoxystyrene[16] with use of the hydrogen iodide/zinc iodide (HI/ZnI_2) initiating system. This series of studies is concerned with the synthesis of end-functionalized poly(*p*-alkoxystyrenes) based on these living cationic processes, to which we applied two methods of end functionalization that had originally been developed for vinyl ethers:[3,4a] In one method (eq 1), living polymerization of a *p*-alkoxystyrene is initiated by an initiator carrying a functional group (X) to be incorporated into the polymer as a "head" (α-end) group (functional initiator method). Herein typical "functional initiators" are the adducts (**2**) of hydrogen iodide with vinyl ethers (**1**) carrying a pendant function X.[2–4] The other method (eq 2) utilizes the quenching of the HI/ZnI_2-initiated living poly(*p*-alkoxystyrene) with a reagent (**7**) having a functional group (Z) to be attached to the polymer "tail" (ω-end) (end-capping method).[4a]



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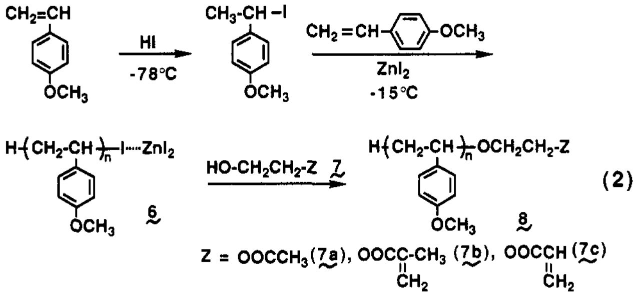

(2)

Although these two methods are identical, in principle, with those for vinyl ethers, their applicability to *p*-alkoxystyrenes is not straightforward and may depend on a few factors. As to the functional initiator method (eq 1), for example, it is unknown whether the vinyl ether derived initiators **2**, coupled with ZnI_2, can indeed initiate (living) cationic polymerization of *p*-alkoxystyrenes, which are less reactive than alkyl vinyl ethers. As to the end-capping method (eq 2), it is unknown which types of nucleophiles are suited for clean and quantitative end-capping upon the growing *p*-alkoxystyryl carbocations, which are less stable, and hence more prone to β-proton elimination by the added quenchers, than the corresponding vinyl ether cations.

The objectives of this first study were to uncover these specific problems for *p*-methoxystyrene (pMOS) and to synthesize a series of end-functionalized poly(pMOS) by the proposed two methods. A wide variety of α- and ω-end functions were examined, as shown in eqs 1 and 2.

Results and Discussion

1. End-Functionalized Poly(pMOS) by Functional Initiator Method. Living Cationic Polymerization.

As illustrated in eq 1, a series of end-functionalized poly-

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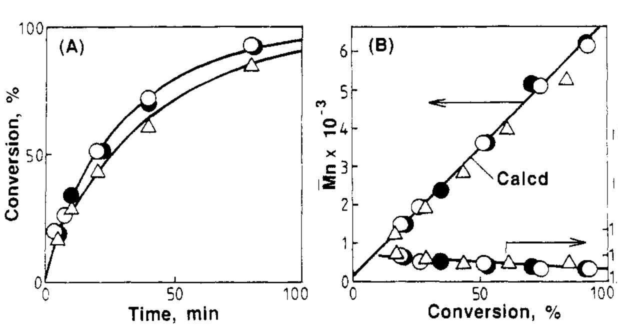


Figure 1. Time–conversion curves (A), and $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ (B) of poly(pMOS) obtained with the X-CH$_2$CH$_2$OCH(CH$_3$)I (2)/ZnI$_2$ initiating systems in toluene at −15 °C. X: (○) OCOCH$_3$; (●) CH(COOC$_2$H$_5$)$_2$; (△) phthalimido. [pMOS]$_0$ = 0.50 M; [2]$_0$ = 10.0 mM; [ZnI$_2$]$_0$ = 5.0 mM. The intercept on the $\bar{M}_n$ axis indicates the molecular weight of pMOS monomer (= 134).

(pMOS) (**4a–c**) were prepared with use of functional initiators (**2a–c**), which were the adducts of hydrogen iodide with vinyl ethers (**1**) carrying functional pendant groups X. Thus, pMOS was polymerized in toluene at −15 °C with the three initiators (**2**) in conjunction with ZnI$_2$ (0.5 equiv to **2**). The functional group X in initiator **2** included acetoxy (**2a**), malonate (**2b**), and imido (**2c**), which are, respectively, the protected forms of hydroxy, carboxy, and amino groups. Despite our recent success in polymerizing pMOS from the HI/ZnI$_2$-generated living poly(vinyl ether),[17] the polymerization of pMOS with an initiator derived from a vinyl ether is not known yet.

Preliminary experiments soon revealed that the initiator **2**, prepared at −78 °C, should be mixed with monomer and then with ZnI$_2$ at the same low temperature. If the adduct, ZnI$_2$, and pMOS are mixed at −15 °C (the polymerization temperature), living poly(pMOS) still forms but its end functionality is below 1.0, apparently because at −15 °C the HI adduct partially releases hydrogen iodide that initiates nonfunctionalized pMOS chains. Thus, all the experiments described herein were carried out by mixing **2**, monomer, and ZnI$_2$ at −78 °C, keeping the reaction mixture at the same temperature for 20 h, and then gradually warming it to −15 °C, where the polymerization occurred.

Figure 1 shows the time–conversion curves, the number-average molecular weight ($\bar{M}_n$) and polydispersity ratio ($\bar{M}_w/\bar{M}_n$) for the polymers obtained with three **2**/ZnI$_2$ initiating systems. The polymerizations proceeded quantitatively, where the overall reaction rates were almost independent of the functional groups X of the initiator **2** (Figure 1A). This fact is consistent with the polymerization pathway shown in eq 1. Namely, regardless of the functional group X of the initiators, all the initiating systems lead to the identical growing active sites, once the initiation has been completed.

The $\bar{M}_n$'s of the polymers increased in direct proportion to monomer conversion and were virtually independent of the kind of initiators. The observed $\bar{M}_n$'s, although determined relative to standard polystyrenes, were in good agreement with the calculated values based on the assumption that one polymer chain forms per unit initiator. In addition, the $\bar{M}_w/\bar{M}_n$ ratios remained unchanged and well below 1.1 at all conversions. These facts show the living nature of the polymerization of pMOS initiated by the **2**/ZnI$_2$ system, despite the polar functional groups X therein.

Polymer Characterization. The end-group structure of the polymers was determined by ^{1}H NMR spectroscopy (see below). Figure 2A depicts the ^{1}H NMR spectrum of a typical sample of the acetoxy-capped poly(pMOS) obtained with **2a**/ZnI$_2$ initiating system. The spectrum exhibits all key absorptions of the poly(pMOS) main chain (a and b), the acetoxy group of the initiator fragment (d, e, and f), and the methoxy terminal (c)[21] that is derived from termination with methanol; absorptions indicative of byproducts resulting from protonic impurities are completely absent. All these observations are consistent with the expected structure of **4a**.

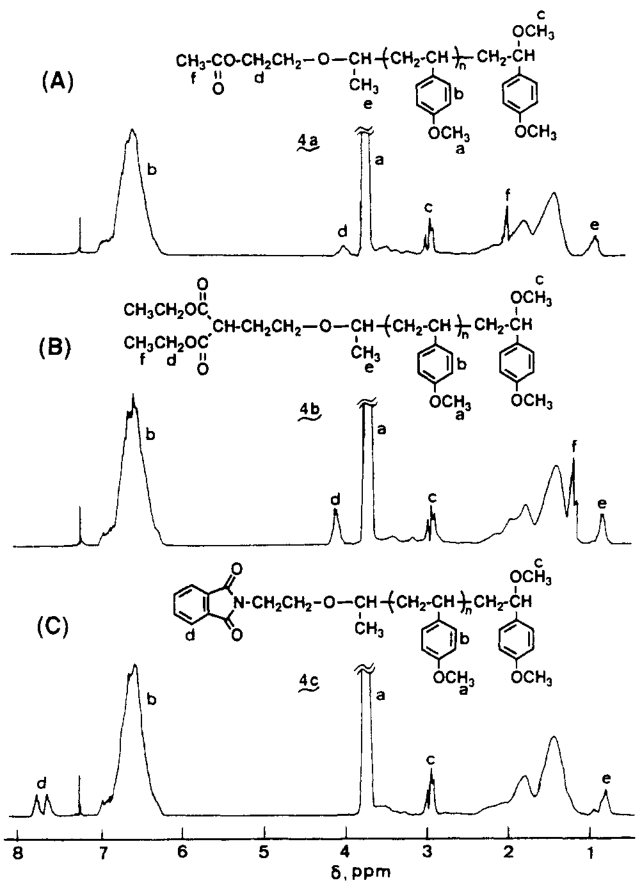


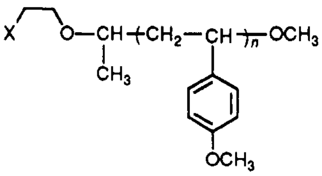
Figure 2. ^{1}H NMR spectra (CDCl$_3$) of end-functionalized polymers: (A) acetoxy-capped poly(pMOS) **4a** (entry 1, Table I); (B) malonate-capped poly(pMOS) **4b** (entry 2, Table I); and (C) imido-capped poly(pMOS) **4c** (entry 3, Table I).

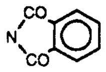
The number-average degree of polymerization ($\overline{DP}_n$) for **4a** was determined from the peak intensity ratio of the pendant methoxy or the phenyl groups to the terminal methoxy (a/c or b/c). As shown in Table I, $\overline{DP}_n$'s were in good agreement with the calculated values ($\overline{DP}_n$ = [pMOS]$_0$(%conv/100)/[**2a**]$_0$), which were based on the assumption that one living chain is formed from one molecule of **2a**. After the living nature of the polymerization (i.e. the absence of chain transfer and termination) had thus been established, the number-average end functionality ($\bar{F}_n$) of the terminal (α-end) acetate for **4a** was determined by comparing its integrated ^{1}H NMR peak areas with that of the ω-end methoxy group (ratio: d/c and e/c). Although determined from the intensity ratios independent of each other, $\bar{F}_n$ was invaluably close to unity, indicating the formation of acetoxy-capped poly(pMOS) **4a** that has exactly one acetate group per chain.

Very similar results were obtained for the polymers (**4b** and **4c**) synthesized with the initiator that carries an ethyl malonate (**2b**) or a phthalimido (**2c**) pendant group. The ^{1}H NMR spectra of **4b** and **4c** are shown in Figure 2, parts B and C, respectively. Table I shows the $\overline{DP}_n$ (obsd) and the $\bar{F}_n$ of these polymers.

End-Group Transformation. As shown in eq 1, the terminal functional groups of the polymers **4a–c** were converted into the corresponding hydroxy (**5a**), carboxy

Table I
Synthesis of End-Functionalized Poly(pMOS) (4 and 5) by the Functional Initiator Method[a]



entry	code	X	$\overline{DP}_n$(calcd)[b]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	$\overline{DP}_n$ (obsd)[d,e]		$\bar{F}_n$[d,f]	
						a/c	b/c	d/c	e/c
1	**4a**	OOCCH$_3$	13.2	1960	1.08	13.5	13.6	0.99	1.01
	5a	OH		1830	1.10				
2	**4b**	CH(COOEt)$_2$	14.0	2120	1.09	14.1	14.3	0.99	0.99
	5b	CH$_2$COOH		1900	1.11				
3	**4c**		14.5	1850	1.12	14.5	14.6	0.96	0.99
	5c	NH$_2$		1720	1.15				

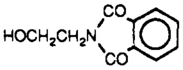
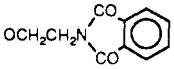
[a] Polymerization was sequentially carried out in toluene at −78 °C (24 h) and −15 °C (10 min). [pMOS]$_0$ = 0.50 M; [**2**]$_0$ = 10 mM; [ZnI$_2$]$_0$ = 5.0 mM. [b] $\overline{DP}_n$(calcd) = (% conv/100)[pMOS]$_0$/[**2**]$_0$. [c] Measured by SEC. [d] ^{1}H NMR peak intensity ratio; see Figure 2. [e] Number-average degree of polymerization. [f] Number-average end functionality.

(**5b**), and amino (**5c**) terminals. Thus, for example, a sample of **4a** (shown in Figure 2A) was hydrolyzed under mild alkaline conditions (see the Experimental Section). The signals d and f, associated with the acetate terminal (4.10 and 2.05 ppm, respectively; see Figure 2A) are absent in the hydrolysis product, indicating the formation of the hydroxy-capped poly(pMOS) **5a**.[5] The structure, $\overline{DP}_n$, and MWD of the poly(pMOS) backbone remained unchanged during the end-group transformation, as seen in Table I.

In a similar manner, the α-end malonate of **4b** was converted into the corresponding carboxy group by the alkaline hydrolysis, followed by thermal decarboxylation.[4a] The signals associated with the malonate terminal (1.25 and 4.15 ppm; see Figure 2B) are absent in the hydrolysis/decarboxylation product, indicating the formation of the carboxy-capped poly(pMOS) **5b**. Furthermore, **4c** was hydrazinolyzed, where the peak d due to the imido terminal (7.70 ppm; see Figure 2C) disappeared, to give the amino-capped poly(pMOS) **5c**.[6] The data shown in Table I (entries 1–3) corroborate that the poly(pMOS) backbones of these polymers were kept intact during the transformation processes.

2. End-Functionalized Poly(pMOS) by End-Capping Method. Search of End-Capping Agents. In the second part of this study, end-functionalized poly(pMOS) was synthesized by the end-capping method using "functional" capping agents (cf. eq 2). As reported previously, some delocalized carbanions (malonate[4,5] and phenyl[5]) and enolates[11] react quantitatively with living poly(vinyl ether) growing ends to give stable terminal groups, but it remains unknown, in general, which types of basic compounds are suited for living poly(pMOS) ends. The criteria for these quenchers include (a) quantitative attachment to a polymer end, (b) absence of side reactions such as β-proton elimination, and (c) formation of stable terminal groups. In this regard, a wider variety of capping agents may be applicable to poly(pMOS) than to poly(vinyl ethers). In particular, alcohols and amines are not best suited for the latter polymers because they lead to rather unstable acid-sensitive acetal and amino ether terminals, respectively, but such problems are not relevant to poly(pMOS).

Table II
End-Capping Reactions of Living Poly(pMOS) with Various Capping Agents[a]

entry	capping agent	end group	$\bar{F}_n$[b]
4	NaCH(COOC$_2$H$_5$)$_2$	CH(COOC$_2$H$_5$)$_2$	0
5	HOC(CH$_3$)$_3$	OC(CH$_3$)$_3$	0
6	HOCH(CH$_3$)$_2$	OCH(CH$_3$)$_2$	0.98
7	HOCH$_3$	OCH$_3$	0.99
8	HOCH$_2$CH$_2$OOCCH$_3$	OCH$_2$CH$_2$OCOCH$_3$	0.98
9	HOCH$_2$COOCH$_3$	OCH$_2$COOCH$_3$	0
10			0.82

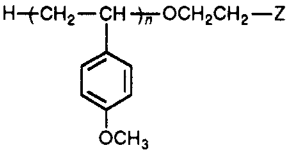
[a] Polymerization by HI/ZnI$_2$ in toluene at −15 °C; [pMOS]$_0$ = 0.38 M; [HI]$_0$ = 19 mM; [ZnI$_2$]$_0$ = 6.0 mM; conversion ~100%; [capping agent]$_0$ ≥ 190 mM. Capping agents were added neat to the reaction mixtures, except for entries 4 and 10, where sodiomalonic ester and 2-(hydroxyethyl)phthalimide were employed as 1,4-dioxane solutions. [b] $\bar{F}_n$ = [end group]/[α-CH$_3$] by ^{1}H NMR.

With these points in mind, we first examined sodiomalonic ester (carbanion salt) and a series of alcohols (primary, secondary, and tertiary) as possible capping agents for a pMOS (Table II). Thus, living cationic polymerization of pMOS was carried out with use of the HI/ZnI$_2$ initiating system in toluene at −15 °C,[15] and near at 100% conversion, it was terminated by adding a solution of a capping agent in a large excess over the living ends (usually, [living end]/[capping agent] = 1/50). The number-average end functionality ($\bar{F}_n$) of the ω-end was determined by comparing ^{1}H NMR peak intensity ratios of the methyl protons (Figure 2A, peak e; arising from the hydrogen iodide initiator) to the protons of the ω-end (Table II); under our conditions, the polymerization by HI/ZnI$_2$ is living and the number of living polymer chains is equal to that of HI.[15]

As shown in Table II, among the four basic compounds employed in our primary search (entries 4–7), sodiomalonic ester and *tert*-butyl alcohol did not react with the growing end, whereas the primary and the secondary alcohols (methanol and 2-propanol, respectively) underwent quantitative reactions to give alkoxy terminals. The ineffectiveness of the malonate anion is in sharp contrast to its clean attachment to living poly(vinyl ether) ends; the results for the three alcohols indicate that the bulky tertiary alcohol cannot react with the relatively crowded poly(pMOS) cation carrying a phenyl and a polymer backbone.

On the basis of these results, we then examined, as functional capping agents, three primary alcohols that carry protected forms of hydroxy, carboxy, and amino functions (entries 8–10). Although having essentially the same alcoholic moieties, however, only 2-hydroxyethyl

Table III
Synthesis of End-Functionalized Poly(pMOS) (8) by the End-Capping Method[a]



entry	code	Z[a]	$\overline{\mathrm{DP}}_n$(calcd)[b]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	$\overline{\mathrm{DP}}_n$(obsd)[d,e] a/c	$\overline{\mathrm{DP}}_n$(obsd)[d,e] b/c	$\bar{F}_n$[d,f] d/c	$\bar{F}_n$[d,f] e/c	$\bar{F}_n$[d,f] f/c
11	**8a**	$OOCCH_3$	23.8	2910	1.07	23.6	23.7	0.98		
12	**8b**	$OOCC(CH_3){=}CH_2$	18.9	2560	1.07	19.0	19.1	1.00	0.98	
13	**8c**	$OOCCH{=}CH_2$	16.9	2330	1.07	16.7	16.6	1.03	0.98	0.99

[a] Polymerizations were carried out in toluene at −15 °C. $[\mathrm{pMOS}]_0 = 0.50$ M; $[\mathrm{HI}]_0 = 21$–30 mM; $[\mathrm{ZnI_2}]_0 = 5.0$ mM; conversion ~ 100%. Capping agents ($HOCH_2CH_2$-Z): neat; $[HOCH_2CH_2\text{-}Z]_0/[\mathrm{HI}]_0 \geq 10$. [b] $\overline{\mathrm{DP}}_n$ (calcd) = $[\mathrm{pMOS}]_0/[\mathrm{HI}]_0$. [c] Measured by SEC. [d] ^{1}H NMR peak intensity ratio; see Figure 3 and text. [e] Number-average degree of polymerization. [f] Number-average end functionality.

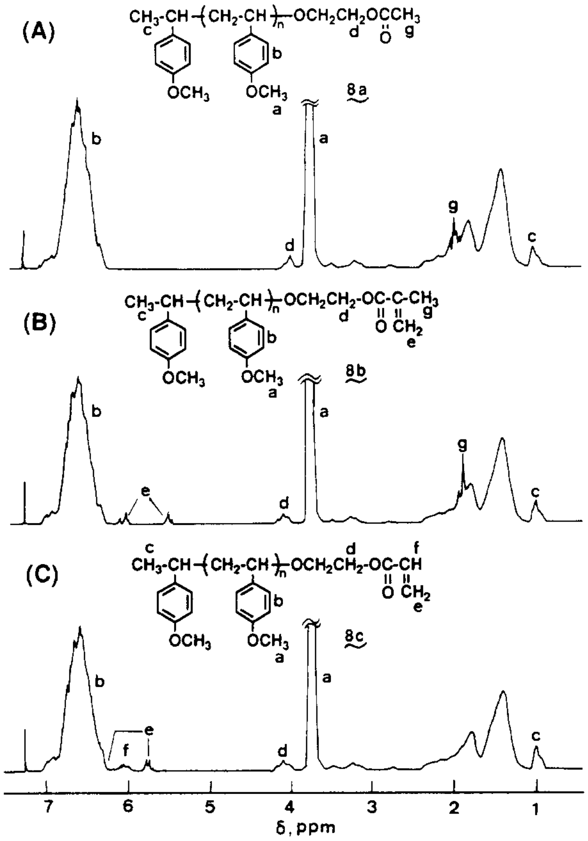


Figure 3. ^{1}H NMR spectra ($CDCl_3$) of end-functionalized polymers: (A) acetoxy-capped poly(pMOS) **8a** (entry 11, Table III); (B) methacryloxy-capped poly(pMOS) **8b** (entry 12, Table III); and (C) acryloxy-capped poly(pMOS) **8c** (entry 13, Table III).

acetate underwent a quantitative end-capping (entry 8); methyl hydroxyacetate was totally ineffective at all (entry 9); and 2-hydroxyethyl phthalimide resulted in a partial attachment only. In all these cases, however, there were no side reactions due to the functional groups in the capping agents. Thus, the inertness of methyl hydroxyacetate probably results from the electron-withdrawing α-carbonyl that substantially reduces the basicity of the hydroxyl group.

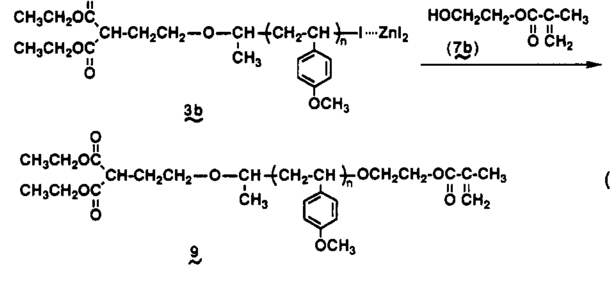
Consequently, we have decided to employ a series of β-substituted ethanol derivatives as primary alcoholic capping agents. Thus, the HI/ZnI_2-initiated living poly(pMOS) was terminated with three kinds of 2-hydroxyethyl carboxylates: acetate (**7a**), methacrylate (**7b**), and acrylate (**7c**). All polymers showed a very narrow MWDs ($\bar{M}_w/\bar{M}_n < 1.1$; see Table III, entries 11–13).

Figure 3 shows the ^{1}H NMR spectra of these polymers. For example, a typical spectrum of the polymer obtained with **7a** is given in Figure 3A. All key absorptions of both "head" methyl (peak c) and "tail" acetoxy (peaks d and g) groups are seen, confirming the structure expected for polymer **8a**. The ratio of the "head" methyl protons (peak c) to the main-chain methoxy or phenyl protons (a/c or b/c) gave the observed $\overline{\mathrm{DP}}_n$, which proved almost equal to the value calculated from the pMOS/HI (initiator) feed ratio. The $\bar{F}_n$ of **8a** was obtained from the ratio of the "head" methyl protons to the methylene protons of the "tail" oxyethyl acetate group (d/c) and was almost equal to unity (Table III, entry 11).

Very similar results were obtained for the polymers prepared with other functional primary alcohols (**7b** and **7c**). Quantitative formation of polymers **8b** (methacryloxy end) and **8c** (acryloxy end) were confirmed by ^{1}H NMR analysis (Figure 3, parts B and C); the $\bar{F}_n$'s were all close to unity (Table III, entries 12 and 13). These facts indicate that end-functionalized poly(pMOS) can be synthesized not only by the functional initiator method (eq 1) but by the end-capping method (eq 2) as well.

Living cationic polymers of vinyl ethers ($CH_2{=}CH{-}OR$) can be terminated by some alcohols (R′OH) quantitatively to give an alkoxy-capped polymer,[4d] but the resulting end group is an acetal [~~~CH(OR)(OR′)] which is chemically unstable under acidic conditions. In contrast, for poly(alkoxystyrene)s, quenching with an alcohol leads to a chemically stable alkoxy end (ω-end), and this in turn permits the synthesis of poly(pMOS) with a great variety of end-functional groups. In particular, **8b** and **8c** are new attractive macromonomers with an anionically and radically polymerizable methacryloxy group.

3. Heterotelechelic Poly(pMOS). As applied to poly(vinyl ether)s previously,[2] combination of the functional initiator method and the end-capping method, i.e., quenching the living polymer with alcohol **7**, led to heterotelechelic polymers (eq 3). For example, living poly(pMOS) **3b**



(3)

was prepared with the **2b**/ZnI_2 initiating system (eq 1), and its living end was subsequently end-capped in situ

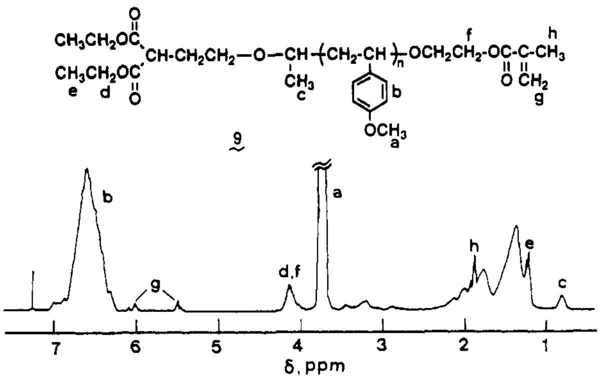


Figure 4. ^{1}H NMR spectrum ($CDCl_3$) of malonate–methacryloxy heterotelechelic poly(pMOS) **9**.

with excess 2-hydroxyethyl methacrylate (**7b**) to give polymer **9** ($\bar{M}_n$ = 2600, $\bar{M}_w/\bar{M}_n$ = 1.08, by size-exclusion chromatography).

The heterotelechelic structure (**9**) of the products was established by ^{1}H NMR spectroscopy (Figure 4). The spectrum exhibits absorptions of the "head" ethyl malonate (peaks d and e) and the "tail" methacrylate (peaks f, g, and h) protons. The ratio of the "head" methyl protons (peak c) to the main-chain protons (a/c or b/c) gave $\overline{DP}_n$, which was almost equal to the calculated value [e.g., (obsd) 21.2 (from a/c), 21.4 (from b/c); (calcd) 2.1].

The number-average end functionalities were determined from the peak intensity ratio of the "head" malonate and the "tail" methacrylate groups to the initial methyl group arising from the initiator: $\bar{F}_n$ (malonate) = d/c; $\bar{F}_n$ (methacrylate) = g/c. Both $\bar{F}_n$ (α) (= 0.99) and $\bar{F}_n$ (ω) (= 1.01) are close to unity, indicating the quantitative attachment of one malonate and one methacrylate group per polymer molecule.

Experimental Section

Materials. Commercial pMOS (Fluka) was washed with an aqueous alkali solution and then water, dried overnight over anhydrous sodium sulfate, and distilled twice over calcium hydride under reduced pressure. Functionalized vinyl ethers **1** (2-acetoxyethyl vinyl ether,[16] diethyl 2-(vinyloxy)ethyl malonate,[17] and 2-(vinyloxy)ethyl phthalimide[4]) were synthesized as reported, and these were purified by double distillation over calcium hydride under reduced pressure. The gas chromatographic purity of those monomers all exceeded 99.8%. Capping agents [2-hydroxyethyl acetate (**7a**), 2-hydroxyethyl methacrylate (**7b**), 2-hydroxyethyl acrylate (**7c**), methanol, 2-propanol, and *tert*-butyl alcohol; all from Wako Chemicals, purity > 99%] were used without further purification. Anhydrous hydrogen iodide was prepared as an *n*-hexane solution as described.[18] ZnI_2 (Aldrich, purity > 99.99%) was used as received; it was vacuum-dried overnight just before use and handled in the dark under dry nitrogen.[19] Toluene (polymerization solvent), diethyl ether (solvent for ZnI_2), and tetrahydronaphtalene (internal standard for gas chromatography) were purified by the usual methods[8] and distilled twice over calcium hydride just before use.

Procedures. Polymerizations were carried out under dry nitrogen in a baked glass vessel equipped with a three-way stopcock.[19] When adduct **2** was used an initiator (eq 1), vinyl ether **1** was first treated with an equimolar amount of hydrogen iodide in *n*-hexane at −78 °C. To this solution of **2** were added pMOS monomer and ZnI_2 solution in this order to keep the same temperature for 20 h, and the mixture was transferred to a methanol bath kept at −15 °C to initiate polymerization. When HI was used as an initiator, precooled solutions of hydrogen iodide (in *n*-hexane) and zinc iodide (in diethyl ether) were added successively in this order to a monomer solution (in toluene). The living polymerizations were terminated by adding prechilled ammoniacal methanol or capping agents (see Tables I–III).

The quenched reaction mixtures were sequentially washed with 10% aqueous sodium thiosulfate solution and with water, evaporated to dryness under reduced pressure, and vacuum-dried to give the product polymers.

pMOS conversion was determined from its residual concentration measured by gas chromatography with tetrahydronaphthalene as an internal standard.

Polymer Characterization. The structure and the $\overline{DP}_n$ of the polymers were determined by ^{1}H NMR spectroscopy (270 MHz) at +40 °C in $CDCl_3$ on a JEOL GSX-270 spectrometer (see the Results and Discussion section). The molecular weight distribution (MWD) of the products was determined by size-exclusion chromatography (SEC) in chloroform at room temperature on a JASCO Trirotar chromatograph equipped with polystyrene gel columns (Shodex K-802, K-803 and K-804; 8.0 mm i.d. × 300 mm each) and refractive index/ultraviolet dual detectors. The polydispersity ratio ($\bar{M}_w/\bar{M}_n$) were calculated from size-exclusion eluograms on the basis of a polystyrene calibration.

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References and Notes

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(21) The methoxy absorption (c) is split into two singlets due to the stereoisomerism of the terminal methine carbon to which it is attached.