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End-Functionalized Polymers by Living Cationic Polymerization. 1. Mono- and Bifunctional Poly(vinyl ethers) with Terminal Malonate or Carboxyl Groups

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ABSTRACT: Terminally mono- and bifunctional monodisperse poly(vinyl ethers) I–III, carrying malonic ester, its sodium salt, or the corresponding carboxylic acid as terminal function X, were synthesized by living cationic polymerization of vinyl ethers by the hydrogen iodide/iodine initiating system [$CH_3CH(OCH_2CH_2X)–(CH_2CH(OR))_n–OCH_3$ (I), $H–(CH_2CH(OR))_n–X$ (II), $CH_3CH(OCH_2CH_2X)–(CH_2CH(OR))_n–X$ (III) ($X = CH(COOC_2H_5)_2, CH(COONa)_2, CH_2COOH$; $R = CH_3, CH_2CH(CH_3)_2$)]. The backbone polymers were hydrophilic poly(methyl vinyl ether) and lipophilic poly(isobutyl vinyl ether). Two methods were employed for the synthesis of the monofunctional malonate-capped polymers: (1) (for type I) living polymerization of vinyl ethers initiated by a vinyl ether–hydrogen iodide adduct $CH_3CHIOCH_2CH_2CH(COOC_2H_5)_2$ (a functional initiator) in the presence of iodine; and (2) (for type II) end-capping of living poly(vinyl ether), obtained by the hydrogen iodide/iodine initiating system, with the malonate anion $^-CH(COOC_2H_5)_2$. Combination of the two methods gave telechelic malonate polymers of type III. The malonic ester terminals of I–III could be transformed into the corresponding carboxylic acids by base-catalyzed hydrolysis followed by decarboxylation. The end functionalities of these mono- and bifunctional polymers were close to 1 and 2, respectively, according to ^1H NMR analysis and/or conductometric titration.

Introduction

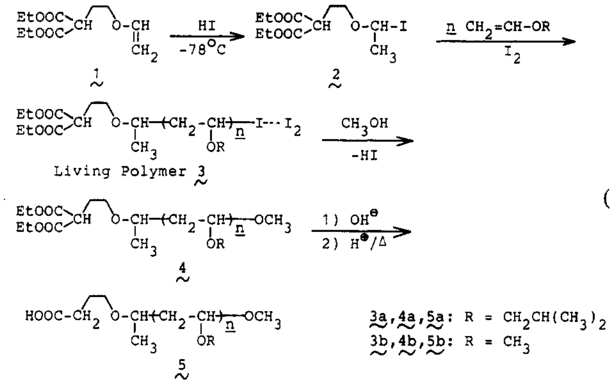
End-functionalized polymers are indispensable building blocks for advanced polymeric materials with specific functions now strongly demanded in many fields. For their usefulness and versatility, they should satisfy at least two criteria: perfect end functionality (exactly one or two terminal functional groups per chain) and controlled molecular weight [or narrow molecular weight distribution (MWD)]. Among a number of possible methods for the synthesis of such polymers, "living" polymerization is no doubt most attractive and straightforward.

The synthesis of end-functionalized polymers via living polymerization usually involves two approaches. In one approach, living polymerization is initiated by an initiator carrying a functional group that is in turn incorporated into the polymer chain end as the "head" group (functional initiator method). The other approach utilizes quenching of living polymer ends with a reagent having a functional group that is attached to the polymer "tail" via a substitution reaction (end-capping method). Although both methods have successfully been employed in anionic and ring-opening cationic polymerizations, where well-established living processes are available,[1] they have found few applications in cationic polymerization of vinyl monomers, primarily because of the dearth of living systems in this field.

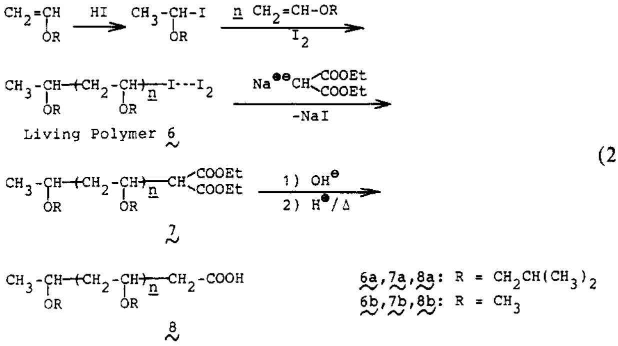
This series of investigations is directed toward the synthesis of end-functionalized polymers via living cationic polymerizations of vinyl monomers initiated by the hydrogen iodide/iodine (HI/I_2) system, which have recently been developed in our laboratories.[2,3] The two features of these living processes, relevant to our purpose, are their initiation mechanism and the stability of the propagating species. According to our recent mechanistic study,[4] the initiation process involves a quantitative addition of hydrogen iodide across the vinyl ether double bond to form an adduct $CH_3CH(OR)I$ which, in the presence of iodine, initiates living propagation. This mechanism implies that an appropriate HI–vinyl ether adduct may serve as a functional initiator. The stability of the propagating species generated by HI/I_2 initiator may allow a clean end-capping free from undesirable side reactions, particularly the β-proton elimination that often accompanies reactions of unstable carbocations with nucleophiles (see eq 4).

This paper, the first of our series, concerns the synthesis of terminally mono- and bifunctional poly(vinyl ethers) carrying malonic ester or carboxyl groups.

Strategy of the Synthesis. Our strategy was based on a combination of the classical malonic ester synthesis with the HI/I_2-initiated living cationic polymerization, coupled with a functional initiator method (eq 1) or an end-capping method (eq 2) or both (eq 3):



(1)



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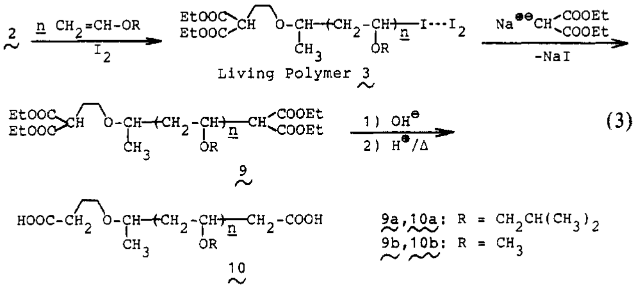


(3)

All these polymers are novel end-functionalized poly(vinyl ethers) with a perfect end functionality ($\bar{F}_n$ = 1.0 or 2.0 ± 0.1), controlled molecular weight, and monodisperse MWD. Recently, we prepared macromers by a functional initiator method and an end-capping method similar to eq 1 and 2, respectively.[5,6]

As vinyl ethers ($CH_2{=}CHOR$) for the backbone polymers, hydrophilic methyl vinyl ether (MVE; R = Me) and lipophilic isobutyl vinyl ether (IBVE; R = *i*-Bu) were employed. Depending on the structure of the backbone and the number of the terminal functional groups per chain, our end-functionalized poly(vinyl ethers) exhibited interesting solubility characteristics.

Results and Discussion

Monofunctional Polymers by Functional Initiator Method. Monofunctional malonate-capped polymer 4 was prepared via the synthesis route illustrated in eq 1. Thus, for example, IBVE was polymerized in CH_2Cl_2 at −15 °C by a functional initiator 2 in conjunction with a catalytic amount of iodine. Initiator 2 is an adduct between hydrogen iodide and vinyl ether 1 (eq 1), carrying a malonic ester function in the pendant that is in turn incorporated into the "head" group of the resulting polymers. The polymerization by the $2/I_2$ initiating system was rapid and complete within 4 min, as is the HI/I_2-initiated living process otherwise under the same conditions.[7,8]

Figure 1 shows the MWD of two polymer samples obtained after quenching the reaction with ammoniacal methanol (cf. eq 1). Both polymers exhibited a very narrow MWD ($\bar{M}_w/\bar{M}_n \leq 1.1$), and their molecular weights ($\bar{M}_n$) could be controlled by regulating the feed ratio of IBVE monomer to 2 (see below). The molecular weights of the samples shown in Figure 1 were deliberately kept rather low for easy characterization; monodisperse polymers of higher molecular weights can be prepared by reaction 1 (and the other two processes, eq 2 and 3, in this study). These facts indicate the living nature of the polymerization initiated by the $2/I_2$ system.

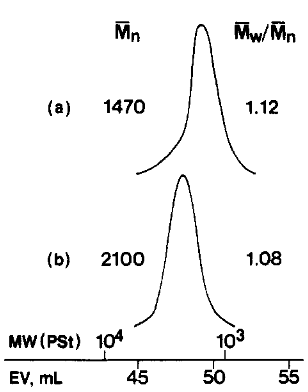


Figure 1. MWD of monofunctional malonate-capped poly(IBVE) 4a obtained by reaction 1 in CH_2Cl_2 at −15 °C: (a) $[IBVE]_0$ = 0.19 M, $[2]_0$ = 24.5 mM, $[I_2]_0$ = 0.20 mM, 4 min, conversion 98%; (b) $[IBVE]_0$ = 0.38 M, $[2]_0$ = 22.4 mM, $[I_2]_0$ = 0.20 mM, 7 min, conversion 97%.

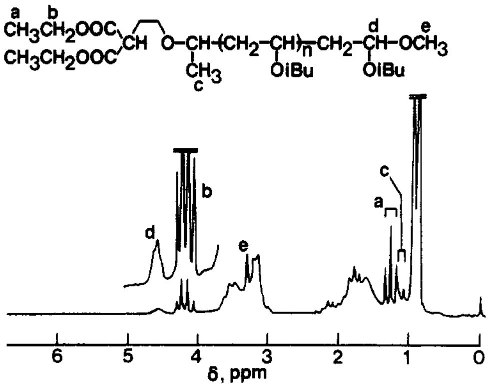


Figure 2. ^1H NMR spectrum (in $CDCl_3$) of monofunctional malonate-capped poly(IBVE) 4a (sample a, Figure 1): $\overline{DP}_n$ = 7.4 (obsd), 7.6 (calcd).

The end-group structure of the polymers (samples a and b; Figure 1) was determined by ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectrum of sample a is given in Figure 2, along with peak assignments. All key absorptions of both "head" malonate (peaks a–c) and "tail" acetal (peaks d and e) groups are seen, confirming the structure expected for polymer 4a. The intensity ratio of peak d [$CH(O\text{-}i\text{-}Bu)CH_3$] to peak b ($COOCH_2$) was very close to the theoretical value (d/b = 1/4). Structure 4a was also established by ^{13}C NMR analysis; e.g., the carbonyl carbons of the malonate terminal were detected at δ 169.1.

The number-average degree of polymerization ($\overline{DP}_n$) of 4a was determined from the peak intensity ratio of the main-chain protons (δ 2.8–3.5) to the terminal methylene protons (peak b). The observed $\overline{DP}_n$ values were in good agreement with the calculated values based on the IBVE/initiator (2) feed ratio: sample a, 7.4 (obsd) vs. 7.6 (calcd); sample b, 16.4 (obsd) vs. 16.6 (calcd).

These results show the formation of malonate-capped poly(IBVE) 4a that has exactly one malonate group per chain, a narrow MWD ($\bar{M}_w/\bar{M}_n$ < 1.1), and a molecular

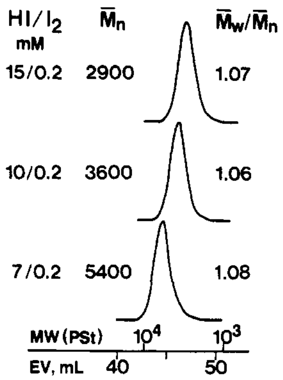


Figure 3. MWD of monofunctional malonate-capped poly(IBVE) **7a** obtained by reaction 2 in CH_2Cl_2 at -15 °C: $[IBVE]_0 = 0.38$ M, conversion ca. 100%; initiator concentrations as indicated.

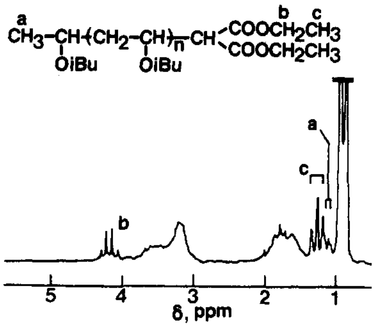


Figure 4. ^1H NMR spectrum (in $CDCl_3$) of monofunctional malonate-capped poly(IBVE) **7a** obtained by reaction 2 in CH_2Cl_2 at -15 °C: $[IBVE]_0 = 0.19$ M, $[HI]_0 = 24.5$ mM, $[I_2]_0 = 0.20$ mM; 4 min, conversion ca. 100%. $\overline{DP}_n = 7.7$ (obsd), 7.8 (calcd); $\bar{M}_w/\bar{M}_n = 1.07$.

weight regulated by the monomer-to-initiator feed ratio. Similarly, poly(MVE) with a malonate terminal was prepared by the living MVE polymerization initiated by the $2/I_2$ system. Polymers **4a** and **4b** could readily be converted into their carboxylic acid forms **5a** and **5b**, respectively (see below).

Monofunctional Polymers by End-Capping Method. Malonate-capped poly(IBVE) (**7a**) and poly(MVE) (**7b**) were also synthesized by the end-capping method using sodiomalonic ester as a capping agent (eq 2). The malonate anion $^-CH(COOEt)_2$ was found to undergo a quantitative substitution reaction onto the active end of living poly(vinyl ether) **6** to give **7** with a malonate "tail" group. As a typical example, the synthesis of **7a** is discussed in this section.

The initial step of the synthesis was the now-established living polymerization of IBVE by HI/I_2 initiator in CH_2Cl_2 at -15 °C.[7,8] When the reaction was almost completed (t = 4 min, IBVE conversion ca. 100%), it was terminated by adding sodiomalonic ester in 4–6-fold excess over the living ends, the concentration of which is equal to that of hydrogen iodide. The immediate precipitation of sodium iodide indicated a successful end-capping process.

Figure 3 illustrates the MWD of the polymers thus obtained at three HI concentrations. All the MWDs are quite narrow, with $\bar{M}_w/\bar{M}_n$ well below 1.1 and shifting toward higher molecular weight with decreasing HI concentration. These facts support a rapid quenching of the living ends with the malonate carbanion.

Structural analyses of the polymers by ^1H and ^{13}C NMR spectroscopy confirmed the structure expected for **7a**. For example, their typical ^1H NMR spectrum (Figure 4)clearly showed the methylene (peak b) and methyl (peak c) signals of the malonate "tail" group, along with the absorption

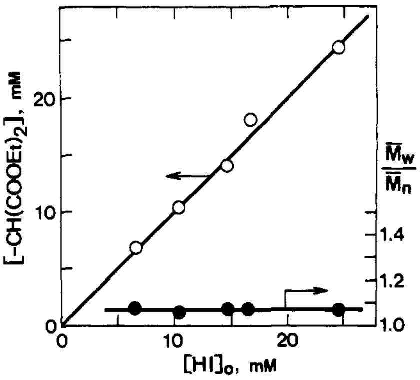


Figure 5. Concentration of the terminal malonate group and $\bar{M}_w/\bar{M}_n$ ratio for monofunctional poly(IBVE) **7a** as a function of the initial HI concentration $[HI]_0$: polymerizations in CH_2Cl_2 at -15 °C; $[IBVE]_0 = 0.38$ M, $[I_2]_0 = 0.20$ mM, conversion ca 100%.

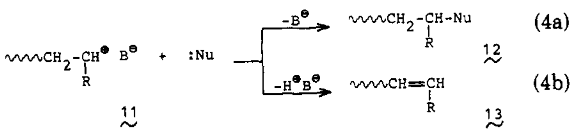
(peak a) due to the "head" methyl group $CH_3CH(O\text{-}i\text{-}Bu)$. The terminal ester carbonyl carbons were also detected by ^{13}C NMR at δ 167.4. Absorptions indicative of byproducts and olefinic terminals (see below) were completely absent in both ^1H and ^{13}C NMR spectra.

The ratio of the terminal methylene protons (peak b) to the main-chain protons (δ 2.9–3.8) gave $\overline{DP}_n = 7.7$, almost equal to the value (7.8) calculated from the IBVE/HI (initiator) feed ratio.

Figure 5 plots the amount (in mol/L) of the terminal malonate groups in the polymer, determined by ^1H NMR, as a function of $[HI]_0$, the initial concentration of hydrogen iodide (=living end concentration). The observed malonate concentrations are all equal to $[HI]_0$ within experimental error over the whole range examined, and this agreement shows a perfect end functionality of polymer **7a** (one malonate end group per chain). Equally important, the MWD of the polymers was nearly monodisperse ($\bar{M}_w/\bar{M}_n < 1.1$; Figure 5) independent of $[HI]_0$.

Poly(MVE) **7b** capped with a malonate terminal was prepared and fully characterized in a similar manner as above; its perfect end functionality was also confirmed by ^1H and ^{13}C NMR analysis.

In cationic polymerization of vinyl monomers, in general, the propagating species (**11**; eq 4) undergoes two reactions when treated in situ with a nucleophile (:Nu); i.e., an S_N2-type coupling with the nucleophile to give end-capped polymer **12** (eq 4a) and an E2-type abstraction of its β-proton to lead to a terminally unsaturated polymer **13** (eq 4b):



The synthesis of terminally functionalized polymers via the end-capping reaction 4a has often been disturbed by the frequent occurrence of accompanying elimination reaction 4b, because the growing carbocation **11** is usually very unstable, particularly when Lewis acids are initiators. The absence of olefinic terminals in our malonate-capped polymers, as shown in Figures 4 and 5, demonstrates the clean and selective attachment of the malonate anion onto the HI/I_2-initiated living polymer ends.

Telechelic Malonate Polymers. The successful synthesis of monofunctional, malonate-capped polymers **4** and **7** by both the functional initiator method and the end-capping method, discussed above, prompted us to prepare telechelic malonate polymers **9** by reaction 3 (see Intro-

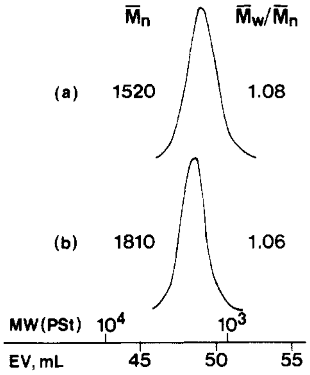


Figure 6. MWD of (a) telechelic poly(IBVE) **9a** and (b) telechelic poly(MVE) **9b** obtained by reaction 3 in CH_2Cl_2. Synthesis conditions: (a) $[IBVE]_0 = 0.19$ M, $[2]_0 = 24.5$ mM, $[I_2]_0 = 0.20$ mM, -15 °C, 4 min, conversion 99%; (b) $[MVE]_0 = 2.4$ M, $[2]_0 = 43.5$ mM, $[I_2]_0 = 1.0$ mM, -40 °C, 60 min, conversion 55%.

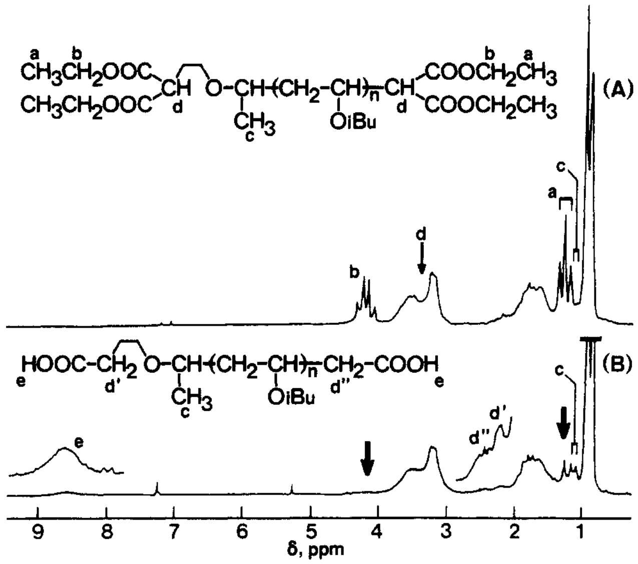


Figure 7. ^1H NMR spectra (in $CDCl_3$) of telechelic poly(IBVE)s: (A) **9a** with malonate ends (sample a, Figure 6), $\overline{DP}_n = 7.0$ (obsd), 7.7 (calcd); (B) **10a** with carboxylic acid ends, obtained from sample A.

duction), in which the two methods are combined. Living polymer **3** carrying a malonate head group was prepared by polymerizing IBVE or MVE with the $2/I_2$ initiating system, and its living end was subsequently end-capped in situ with excess sodiomalonic ester. Figure 6 shows the MWDs of poly(IBVE) and poly(MVE) thus obtained. Both samples exhibit a very narrow MWD ($\bar{M}_w/\bar{M}_n < 1.1$) and their $\bar{M}_n$'s are controllable by regulating the monomer-to-initiator feed ratio, indicating the living nature of the polymerization initiated by the $2/I_2$ system.

The telechelic structure of the products expected from **9** in eq 3 was established by ^1H and ^{13}C NMR spectroscopy. A typical ^1H NMR spectrum of the poly(IBVE) (sample a, Figure 6) is given in Figure 7A. It exhibits absorptions a and b due to the (head and tail) malonic esters along with the head methyl signal c. The intensity ratio of peak b to the main-chain protons (δ 2.9–3.8) gave $\overline{DP}_n$(obsd) = 7.0 for structure **9a**, and this value was in good agreement with the calculated $\overline{DP}_n$ (=7.7) based on the IBVE/**2** molar ratio. The ^{13}C NMR spectrum of the same sample showed two ester carbonyl resonances, providing further evidence for the attachment of two slightly different malonate terminals to one chain: $(EtO\mathit{OC})_2CHCH_2CH_2O-$ (head), δ 169.1; $-CH_2CH(O\text{-}i\text{-}Bu)CH(\mathit{CO}OEt)_2$ (tail), δ 167.3.

Table I
Solubility Characteristics[a] of Bifunctional (Telechelic) Poly(MVE)s ($\overline{DP}_n$ = 5-15)

polymer[b]	toluene	$CHCl_3$	EtOH	H_2O
$(EtOOC)_2CH$〰$CH(COOEt)_2$ (**9b**)	sol	sol	sol	sol
$(NaOOC)_2CH$〰$CH(COONa)_2$	insol	insol	sol	sol
$HOOCCH_2$〰CH_2COOH (**10b**)	insol	sol	sol	sol

[a] Measured on ca. 1% (w/v) solutions at room temperature.
[b] The wavy lines (〰) indicate the poly(MVE) backbone; see eq 3 for detailed structures.

Similarly, polymerization of MVE according to eq 3 led to telechelic poly(MVE) **9b** with a perfect end functionality and a narrow MWD (see below).

Hydrolysis and Decarboxylation of Malonate-Capped Polymers: Synthesis of Carboxyl-Capped Polymers. The terminal malonic esters of polymers **4**, **7**, and **9** were converted into the corresponding carboxyl groups by the standard alkaline hydrolysis followed by thermal decarboxylation (see eq 1–3 and Experimental Section). Thus, treatment of **4**, **7**, and **9** with sodium hydroxide in an ethanol/water mixture (1:1 (v/v)) gave polymers with one or two sodium malonate terminals, which were subsequently transformed into the free diacid forms by neutralization with hydrochloric acid (equivalent to the sodium hydroxide used for the hydrolysis). These reactions were monitored and confirmed by ^1H and ^{13}C NMR spectroscopy. Decarboxylation was then carried out in dioxane at 90 °C [for poly(IBVE) **4a**, **7a**, and **9a**] or in water at 50 °C [for poly(MVE) **4b**, **7b**, and **9b**], to yield monocarboxylic acid forms **5**, **8**, and **10**.

Figure 7B illustrates the ^1H NMR spectrum of the hydrolysis/decarboxylation product obtained from poly(IBVE) **9a** (sample A, Figure 7). Comparison between spectra 7A and 7B shows the complete conversion of the terminal malonic esters into the corresponding (mono)carboxyl groups. For instance, signals a and b in Figure 7A, due to the ethyl groups of the malonate moiety, are absent in Figure 7B (see the two thick arrows), where the acidic protons of the carboxyl end groups are in turn seen around δ 8.6 as broad absorption e. After decarboxylation, peaks d′ and d″, assignable to the methylene protons adjacent to the "head" and "tail" carboxyl groups, respectively, appeared in the region δ 2.0–2.5 (Figure 7B); these methylenes come from the methine units (d, Figure 7A) of the precursor malonate terminals. All other signals, including those of the "head" methyl group (peak c) and the poly(IBVE) backbone, remained unchanged during the end-group transformation.

A similar treatment of precursors **4a** and **7a** yielded monofunctional carboxyl-capped polymers **5a** and **8a**, respectively. Although **4a** has an acetal terminal, which is usually unstable under acidic conditions, ^1H and ^{13}C NMR analyses confirmed it to remain intact even after the decarboxylation in dioxane at 90 °C; e.g., its methine and methoxyl protons (cf. signals d and e in Figure 2, respectively) were clearly detected in the ^1H NMR spectrum of the final products. The stability of the acetal terminal under our conditions was further demonstrated by a model reaction in which acetaldehyde diethyl acetal (1,1-diethoxyethane) was kept at 90 °C in dioxane-d_8 containing glacial acetic acid. Upon prolonged heating for a few hours or longer, the acetal underwent no reactions, according to ^1H NMR analysis.

Malonate-capped poly(MVE)s **4b**, **7b**, and **9b** were also converted into the corresponding carboxylic derivatives **5b**, **8b**, and **10b**, respectively, in a similar manner as described for the poly(IBVE) counterparts.

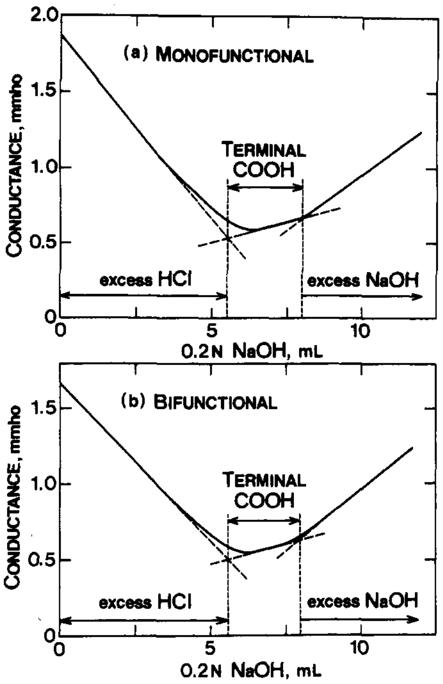


Figure 8. Conductometric titration of carboxyl-capped poly(MVE)s: (a) monofunctional **8b**; (b) telechelic **10b**. (a) 45.6 mg of **8b** in 60 mL of water; $\overline{\mathrm{DP}}_n = 16.3$ ($\bar{M}_n = 1000$), by ^{1}H NMR; $\bar{M}_w/\bar{M}_n = 1.06$; terminal COOH, 5.0×10^{-5} mol (calcd 4.6×10^{-5} mol), $\bar{F}_n = 1.1$. (b) 23.3 mg of **10b** in 60 mL of water; $\overline{\mathrm{DP}}_n = 12.7$ ($\bar{M}_n = 910$), by ^{1}H NMR; $\bar{M}_w/\bar{M}_n = 1.06$; terminal COOH, 4.8×10^{-5} mol (calcd 5.1×10^{-5} mol), $\bar{F}_n = 1.9$. Both solutions were treated with 0.20 N hydrochloric acid (ca. 5 mL) before titration.

Solubility Characteristics. Table I compares the solubility properties of the bifunctional poly(MVE)s (**9b**, its sodium salt, and **10b**) carrying different functional end groups. Because the poly(MVE) backbone is soluble in water and ethanol at room temperature, all these telechelics were soluble in both polar solvents regardless of their terminal groups (malonic ester, sodium malonate, or the corresponding monocarboxylic acid).

However, their solubility in less polar media (chloroform and toluene) did depend on the number and structure of the terminal groups. Thus, diester form **9b** was soluble in both chloroform and toluene, but its sodium salt, having a total of four carboxylate anions, is too polar to be soluble in both of them; note the amphiphilic nature of **9b**, in which lipophilic malonate groups are attached to the hydrophilic poly(MVE) backbone. Telechelic carboxylic acid **10b** exhibits an intermediate solubility, soluble in chloroform but insoluble in toluene. These systematic changes in solubility characteristics also support the clean and quantitative transformation of **9b** to **10b**.

In contrast, the monofunctional polymers (**7b**, its sodium salt, and **8b**) were all amphiphilic and soluble in not only water and ethanol but chloroform and toluene as well.

Because of their lipophilic backbone, the poly(IBVE) derivatives **8a** and **10a** were insoluble in water but soluble in chloroform and toluene.

Conductometric Titration. The solubility in water of the carboxyl-capped poly(MVE)s **8b** and **10b** allowed us to determine their number-average end functionality ($\bar{F}_n$) not only by ^{1}H NMR spectroscopy (see above) but separately by conductometric titration of the terminal carboxylic acids. Figure 8 presents typical examples.

Conductometric titration was carried out on aqueous solutions of **8b** and **10b** that were pretreated with an excess of hydrochloric acid. With increasing added sodium hydroxide, the titration curves exhibited two inflection points, the distance between which corresponds to the amount of the alkali needed to neutralize the terminal carboxylic acids. For the two samples shown in Figure 8, the $\bar{F}_n$ values thus determined were 1.1 for monofunctional **8b** and 1.9 for bifunctional **10b**, both being close to their expected values of 1.0 and 2.0, respectively. Similar results were obtained for other samples of **8b** and **10b** with different $\overline{\mathrm{DP}}_n$.

Experimental Section

Materials. Commercial IBVE was washed sequentially with 10% aqueous sodium hydroxide solution and water, dried overnight over potassium hydroxide pellets, and distilled twice over calcium hydride (gas chromatographic purity >99.8%). Commercial MVE (Tokyo Kasei, purity >99%) was used as received after passing the gaseous monomer through two columns, one packed with potassium hydroxide pellets and the other with granular calcium hydride, just before use.

Sodiomalonic ester for end-capping was used as a solution (0.23 M) in a toluene/dioxane mixture (1.2:1 (v/v)). Thus, in a 100-mL baked flask equipped with a three-way stopcock was added ethyl malonate (1.55 mL, 10.2 mmol) to a suspension of sodium hydride (60 wt % dispersion in mineral oil, 0.40 g, 100 mmol equiv) in toluene (23.5 mL) under dry nitrogen with stirring. With instantaneous evolution of hydrogen, the resulting sodiomalonic ester precipitated as a jelly. Dioxane (20 mL) was added, and the mixture was stirred to give a homogeneous solution, which was kept under dry nitrogen in a refrigerator until used.

Anhydrous hydrogen iodide was obtained as an *n*-hexane solution as described.[3] Iodine was sublimed at 100 °C in the presence of potassium iodide. These initiators were sealed in ampules under dry nitrogen and stored in the dark in a deep freezer. Solvents (toluene, CH_2Cl_2, *n*-hexane, and dioxane) and carbon tetrachloride (as the internal standard for gas chromatography) were purified by the usual methods[3] and distilled at least twice over calcium hydride just before use.

Synthesis of Ethyl (2-(Vinyloxy)ethyl)malonate (1). This was prepared by the substitution reaction of 2-chloroethyl vinyl ether with sodiomalonic ester.[9] In a 300-mL, three-necked, round-bottomed flask equipped with a paddle stirrer and a refulx condenser was carefully dissolved sodium metal (6.3 g, 0.27 mol) in absolute ethanol (150 mL) at room temperature, and ethyl malonate (38 mL, 0.25 mol) and 2-chloroethy vinyl ether (50 mL, 0.50 mol) were added in this order at room temperature. The solution was heated at reflux (ca. 80 °C) with stirring for 5 h, during which period sodium chloride precipitated, and cooled to room temperature. The resulting yellow heterogeneous mixture was evaporated to remove the ethanol, and the red residue was diluted with ether (100 mL). The sodium chloride in the residue was filtered off and extracted with 50 mL of ether. The ether extract was combined with the organic layer, and the mixture was washed with two 100-mL portions of 10% sodium chloride solution, dried overnight with sodium sulfate, and concentrated by evaporating off the ether and unreacted 2-chloroethyl vinyl ether under reduced pressure (40 Torr). The condensed solution was distilled (90 °C (17 Torr)) to remove unreacted ethyl malonate and then doubly distilled in vacuo over calcium hydride to give pure vinyl ether 1 as a colorless oil: yield ca. 30% from ethyl malonate; bp 106 °C (5 Torr); $d^{21}{}_4 = 1.106$; purity >99.8% by gas chromatography; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 6.42 (dd, $J = 6.7$ Hz, $J' = 14.2$ Hz, 1 H, OCH=), 4.20 (q, $J = 7.1$ Hz, 4 H, $COOCH_2$), 4.16 (dd, $J = 2.0$ Hz, $J' = 14.2$ Hz, 1 H, C*H*=CHO, anti, overlapping with the $COOCH_2$ signal), 3.98 (dd, $J = 2.0$ Hz, $J' = 6.7$ Hz, 1 H, C*H*=CHO, syn), 3.75 (t, $J = 6.0$ Hz, 2 H, CH_2OCH=), 3.55 (t, $J = 7.3$ Hz, 1 H, $CH(COOEt)_2$), 2.25 (d of t, $J = 6.0$ Hz, $J' = 7.3$ Hz, 2 H, OCH_2CH_2CH), 1.27 (t, $J = 7.1$ Hz, 6 H, CH_3); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 168.8 (C=O), 151.2 (OCH=), 86.5 (CH_2=), 64.9 (CH_2OCH=), 48.5 ($CH(COOEt)_2$), 28.0 (OCH_2CH_2CH), 13.8 (CH_3).

Polymerization Procedures. Polymerizations were carried out under dry nitrogen in a baked glass vessel equipped with a three-way stopcock.[3] When adduct 2 was used as initiator, 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 monomer and iodine solutions in this order at the same temperature, and the mixture was transferred to a methanol bath kept at −15 or −40 °C to initiate polymerization. For the HI/I$_2$-initiated reactions, hydrogen iodide and iodine solutions were added successively in this order to a monomer solution. The living polymerizations were terminated by adding prechilled ammoniacal methanol or the solution of sodiomalonic ester. In the latter case, the precipitating sodium iodide was subsequently removed by filtration.

The quenched reaction solution was 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.

Hydrolysis and Decarboxylation. Malonate-capped poly(IBVE) (**4a**, **7a**, or **9a**) (0.1 g) was dissolved in ethanol (10 mL), and 5 N sodium hydroxide (5 equiv to the COOEt units in the polymer) was added. The mixture was magnetically stirred for 3 h, water (10 mL) was added, and stirring was continued for an additional 2–3 days. The resulting sodium salt was converted into the malonic acid form by treatment with 6 N hydrochloric acid (5 equiv to the COONa units in the sample). The polymer was isolated by evaporation under reduced pressure, dissolved in dioxane (20 mL), and kept at 90 °C for 1 h for decarboxylation. The product (**5a**, **8a**, or **10a**) was isolated by evaporation, dissolved in CH$_2$Cl$_2$ (50 mL), washed with water to remove the resulting sodium chloride, and then isolated by evaporation followed by vacuum-drying.

Malonate-capped poly(MVE)s **4b**, **7b**, and **9b** were treated in a similar manner, except that the decarboxylation was carried out in water at 50 °C for 24 h and the final products were dissolved in chloroform and washed with warm water at ca. 50 °C.

Polymer Characterization. The MWD of the polymers was determined by size-exclusion chromatography (SEC) in chloroform on a Jasco Trirotar-II chromatograph equipped with three polystyrene columns that were calibrated against at least 10 standard polystyrene samples in the molecular weight range 2×10^2 to 2×10^5.[3] The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values were obtained from SEC eluograms. ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$ or D$_2$O at room temperature on a Jeol FX-90Q instrument.

Conductometric titration was carried out in a glass cell with two platinum-plate electrodes connected to a Wayne Kerr B224 universal bridge. In a typical run, a stirred solution of a polymer sample (20–50 mg) in deionized water (60 mL) was pretreated with 0.2 N hydrochloric acid (5 mL) and then titrated with an 0.2 N sodium hydroxide standard solution.

Registry No. **2**, 7553-56-2; I$_2$, 10034-85-2; HI, 10034-85-2; (EtO$_2$C)$_2$CHNa, 996-82-7.

References and Notes

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(7) We have recently found[8] that the HI/I$_2$-initiated living polymerizations of vinyl ethers proceed in not only nonpolar[3] but polar solvents such as CH$_2$Cl$_2$ as well. In the latter, the polymerization is much faster and requires less iodine (relative to hydrogen iodide), but is otherwise the same as those in *n*-hexane and other nonpolar media.

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Polymerization of New Metallocenylphosphazenes

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ABSTRACT: The polymerization behavior has been examined of four cyclophosphazenes that are bridged by transannular metallocenyl groups. It was found that two ferrocenyl units, one transannular and one pendent, do not block the polymerization process of a fluorocyclotriphosphazene, even though the trimer with only one pendent ferrocenyl group cannot be polymerized. Release of phosphazene ring strain induced by the transannular component appears to be responsible for the difference. A 1,5-transannular ferrocenyl or ruthenocenyl group has a lesser influence on the polymerizability of a phosphazene cyclic tetrameric ring. No evidence was found for a redistribution of monomer units in the conversion of the cyclic oligomers to polymers.

In recent publications,[1-4] we reported the first examples of metallocenylphosphazene high polymers. These were prepared by the ring-opening polymerization of cyclotriphosphazenes to which was linked one ferrocenyl or ruthenocenyl side group, in either a pendent or a transannular configuration. We also reported that the transannular bridging units enhanced the polymerization tendency of phosphazene trimers compared to their counterparts with one pendent metallocenyl side group.[5]

A number of questions arose from that work, including the following: (1) What effect on the polymerization process comes about if both transannular *and* pendent metallocenyl units are attached to the same cyclic trimeric phosphazene ring? (2) Does a polymerization difference result if the pendent component is geminal or nongeminal to the sites of attachment of the transannular linkage? (3) Do phosphazene cyclic *tetramers* that bear a transannular metallocenyl unit polymerize, and if so, what is the structure of the resultant polymers? For example, is there any evidence that repeating units are positionally redistributed as the tetramer is converted to high polymer?

With these questions in mind, we have synthesized the four cyclophosphazenes shown in **1**–**3** and have examined their polymerization behavior.

Results and Discussion

Polymerizations. Compound **1** polymerizes to a soluble macromolecule of type **4** when heated in the molten

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