End-Functionalized Polymers by Living Cationic Polymerization with $EtAlCl_2$. 2. Synthesis of Homo- and Heterotelechelic Poly(isobutyl vinyl ether)[1]

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ABSTRACT: A series of hetero- and homotelechelic polymers $[X—CH_2CH_2OCH(CH_3)[CH_2CH(OiBu)]_nCH(COOC_2H_5)_2$ (3) (X: $OOCCH_3$, $N[COOC(CH_3)_3]_2$, $CH(COOC_2H_5)_2$) and $X—CH_2CH_2OCH(CH_3)[CH_2CH(OiBu)]_nC_6H_5$ (8) (X: $CH(COOC_2H_5)_2$)] of isobutyl vinyl ether (IBVE) were synthesized via living cationic polymerization at a relatively high temperature. The α-end function X was introduced by use of initiating systems where functional trifluoroacetate initiators (2; $X—CH_2CH_2OCH(CH_3)OOCCF_3$), obtained from vinyl ether $X—CH_2CH_2OCH{=}CH_2$, were coupled with $EtAlCl_2$ (activator) and excess 1,4-dioxane (carbocation stabilizer) in n-hexane solvent at 0 and +60 °C. The ω-end functions included malonate and phenyl groups that were introduced by end-capping the resulting living ends with sodiomalonic ester $[NaCH(COOC_2H_5)_2]$ and phenyllithium, respectively. Structural analysis of the products, even obtained at +60 °C, corroborated their controlled molecular weights ($\overline{DP}_n = [IBVE]_0/[2]_0$; $\bar{M}_w/\bar{M}_n < 1.1$) and the attachment of two terminal functions per polymer except for the imide derivative **3b**, for which the end functionality was lower (~60%) at +60 °C. Telechelic polymers (3) could be converted into $[Y—CH_2CH_2OCH(CH_3)[CH_2CH(OiBu)]_nCH_2COOH$ (4) (Y: OH, NH_2, CH_2COOH)], with a hydroxy, amino, or carboxy group at the α-end (Y) and with a carboxy group at the ω-end.

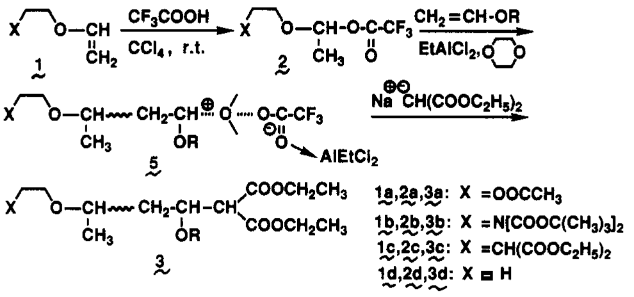
Introduction

Telechelic polymers, indispensable building blocks for advanced polymeric materials, may be prepared by a variety of methods, among which living polymerization is most effective in controlling their molecular weight and end functionality. In a typical synthesis of telechelic polymers, living polymerization is initiated by a bifunctional initiator, and the resulting diheaded living active sites are end-capped with a reagent having a functional group. Although this method is simple to operate, it can afford, by definition, only telechelics that carry the same terminal functions (homotelechelic polymers; X~~~X). In another approach, living polymerization is initiated by an initiator with a functional group (X), followed by quenching the monofunctional living end with a capping agent with another functional group (Y). This method can provide not only homotelechelic polymers (X = Y) but also so-called "heterotelechelic" polymers (X~~~Y; X $\neq$ Y), where the two terminal functions differ from each other.

As we have recently reported,[4,5] terminally monofunctional polymers (5) of vinyl ethers can be synthesized by living cationic polymerization that is initiated with a functional initiator (2) obtained from a vinyl ether (1) with a pendant function X. The living process (Scheme I) is carried out in the presence of ethylaluminum dichloride ($EtAlCl_2$) and a stoichiometric excess of 1,4-dioxane, which are, respectively, an activator for the initiator 2 and a Lewis base for stabilization of the growing carbocation.[6,7] From isobutyl vinyl ether (IBVE), for example, this method affords polymers that carry a "head" functional group X derived from the initiator 2.

The present study was to extend this methodology to the controlled synthesis of homo- and heterotelechelic polymers at relatively high temperatures, up to +60 °C. To this end, the head-functionalized living polymer 5 was quenched with a variety of functional nucleophiles so as to attach a "tail" (ω-end) function. Scheme I illustrates examples of such syntheses where sodiomalonic ester[8,9] is employed as a capping agent to give telechelic polymers 3a–c, which can be converted into more versatile forms (4a–c, respectively; eqs 1–3) with combinations of hydroxy, amino, and carboxy functions. Phenyllithium was also found to be a new end-capping agent that leads to an ω-end phenyl group. Among the reported examples of telechelic polymers of vinyl compounds via living polymerization,[3] there are few of heterotelechelic polymers.

Scheme I



Results and Discussion

1. Survey of End-Capping Agents. As reported previously[4,5] the $2/EtAlCl_2$ initiating system permits truly living cationic polymerization of vinyl ethers. For the synthesis of telechelic polymers via the general route illustrated in Scheme I, we first surveyed end-capping agents that combine quantitatively with the living end (5) without inducing β-proton elimination. Except for sodiomalonic ester,[8,9] it remains unknown which types of nucleophiles are suited for such selective end-capping agents for the living species 5, which is stabilized by an externally added Lewis base (1,4-dioxane) but still involves labile β-protons.

Table I summarizes the results of end-capping experiments with use of six carboanion salts; compounds 6 and 7 are lithium salts of protected alcohols.[10] Despite the frequent use for termination of cationic polymerization, alcohols[8,11,12] and amines[13,14] were excluded from our screening, because, specifically when employed to vinyl

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

capping agent[b]	end group	$\bar{F}_n$[c]
$Li(CH_2)_3CH_3$	$(CH_2)_3CH_3$	0
$Li(CH_2)_3OCH(CH_3)OC_2H_5$ (**6**)	$(CH_2)_3OCH(CH_3)OC_2H_2$	0
$Li(CH_2)_2OSi(CH_3)_3$ (**7**)	$(CH_2)_2OSi(CH_3)_3$	0
LiC_6H_5	C_6H_5	1.01
$BrMgC_6H_5$	C_6H_5	1.00
$NaCH(COOC_2H_5)_2$	$CH(COOC_2H_5)_2$	1.01
		1.00[d]

[a] Polymerization by **2d**/$EtAlCl_2$ in *n*-hexane at 0 °C; $[IBVE]_0$ = 0.38 M; $[\mathbf{2d}]_0 = [EtAlCl_2]_0$ = 20 mM; [1,4-dioxane] = 1.2 M; conversion ~ 100‰ in 15 min; [capping agent] = 200 mM. [b] Added as solution in the following: $Li(CH_2)_3CH_3$, *n*-hexane; **6** and **7**, tetrahydrofuran; LiC_6H_5, cyclohexane/diethyl ether (7/3, v/v); $BrMgC_6H_5$, tetrahydrofuran; $NaCH(COOC_2H_5)_2$, 1,4-dioxane. For all runs, the reaction of the capping agent with the living end was for 60 min. [c] $\bar{F}_n$ = [end group]/$[\mathbf{2d}]_0$ by ^1H NMR; see text. [d] Polymerization at +60 °C.

ethers, these oxygen and nitrogen bases would lead to acetal and amino ether terminals, respectively, which are not very stable under acidic conditions at high temperature. For simplicity, the polymerization for the search of end-capping agents was initiated with a nonfunctionalized initiator **2d** (X: H), which was derived from ethyl vinyl ether, coupled with $EtAlCl_2$ activator in *n*-hexane at 0 or +60 °C in the presence of exess 1,4-dioxane (1.2 M, 10 vol %). Under these conditions, the polymerization was living ([living end] = $[\mathbf{2d}]_0$)[4,5] and reached >95% conversion, at which moment end-capping agents were added (10-fold molar excess over the living end **5**).

The three primary alkyllithium compounds (*n*-butyllithium, **6**, and **7**) turned out totally ineffective as capping agents. Despite the use of a large excess of these salts, no alkyl residues from the lithium compounds were found in the recovered polymers. Although BuLi is expected to abstract the β-hydrogen to give an olefin terminal, no such end group was detected at all in the product by ^1H NMR spectroscopy even under high sensitivity measurement. No further attempt was made to clarify whether or not the living end **5** was terminated by BuLi.

In contrast, the phenyl carbanion (LiC_6H_5 and $BrMgC_6H_5$) and the malonate anion [$NaCH(COOC_2H_5)_2$] instantaneously terminated the polymerization to give poly(IBVE) capped with a phenyl or a malonate group, respectively. ^1H NMR analysis showed the attachment of these end groups even at +60 °C, as discussed later in this paper; i.e., the number-average end functionality $\bar{F}_n$ was invariably very close to unity. Interestingly, these results indicate that delocalized and "soft" carbanions (phenyl and malonate) are better suited than localized and "hard" counterparts (primary carbanions) for end-capping the vinyl ether living end, which may also be relatively "soft" carbocations in nature where the cationic charge is partially delocalized over the α-ether oxygen. In the following part of this study, therefore, sodiomalonic ester and phenyllithium were employed as end-capping agents.

2. Synthesis of X/COOH Telechelic Poly(IBVE) by Malonate End-Capping. (a) End-Capping with Sodiomalonic Ester at High Temperature. Besides the search of suitable end-capping agents for the base-stabilized living end **5**, another focus of this study was to synthesize telechelic poly(vinyl ethers) at temperatures high above ambient temperature where β-proton abstraction from living end by end-capping agents would be more likely to occur. Thus, the end-capping with sodiomalonic ester was examined in detail in the IBVE polymerization with the **2d**/$EtAlCl_2$ system at +60 °C as well as at 0 °C.[15] The recovered polymers gave ^1H NMR spectra identical with those reported for malonate capped poly(IBVE).[8,9] The end functionality $\bar{F}_n$ was determined from the NMR peak intensity ratio of the malonate methylene (4 H, 4.2 ppm) to the poly(IBVE)'s pendant methyl (6 H, 0.9 ppm). No evidence was available for the occurrence of the β-proton abstraction by the sodium salt, even at a temperatures as high as +60 °C.

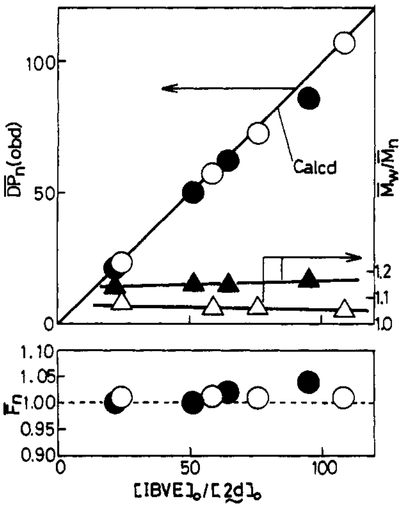


Figure 1. Effect of the initial **2d** concentration ($[\mathbf{2d}]_0$) on the $\overline{DP}_n$(obsd), $\bar{M}_w/\bar{M}_n$, and $\bar{F}_n$ of malonate-capped polymers (**3d**) in the IBVE polymerization by **2d**/$EtAlCl_2$ in *n*-hexane at 0 °C (○,△) and +60 °C (●,▲): $[IBVE]_0$ = 0.76 M; $[\mathbf{2d}]_0$ = 7–35 mM; $[EtAlCl_2]_0/[\mathbf{2d}]_0$ = 1.0 (0 °C) or 0.80 (+60 °C); [1,4-dioxane] = 1.2 M; conversion ~100%.

In addition to the end functionality $\bar{F}_n$, the number-average degree of polymerization [$\overline{DP}_n$(obd)] was determined from the ratio of the pendant methyl to the α-end methyl. Figure 1 plots the $\bar{F}_n$ and $\overline{DP}_n$(obsd) of the polymers produced at different initiator concentrations at 0 and +60 °C (conversion, ca. 100%).

For both temperatures, $\overline{DP}_n$(obsd) was in good agreement with the calculated value (= $[IBVE]_0/[\mathbf{2d}]_0$) for living polymers in the range from 20 to 100. In this range, the MWDs of the products were very narrow ($\bar{M}_w/\bar{M}_n$ < 1.1), though slightly broader at +60 °C. For all these polymers, the end functionality $\bar{F}_n$ was invariably close to unity. Even at +60 °C, therefore, the **2d**/$EtAlCl_2$ initiating system generates living polymers that can be cleanly and quantitatively quenched by sodiomalonic ester to form malonate-capped polymers **3d**.

(b) Synthesis of HO/COOH Heterotelechelic Poly(IBVE) (4a). After establishing the feasibility of end-capping of the base-stabilized living end **5** with the malonate anion, we proceeded to synthesize a series of hetero- and homotelechelic polymers **3** and **4** by this method at 0 °C and even at +60 °C (Scheme I), particularly focusing on its feasibility at high temperature (+60 °C). As an initial example, hydroxy- and carboxy-capped heterotelechelic poly(IBVE) **4a** was prepared. Thus, living IBVE polymerization was initiated with the acetate-functionalized initiating system **2a**/$EtAlCl_2$ [X: $OOCCH_3$] at 0 and +60 °C in *n*-hexane solvent containing 1,4-dioxane, and the resultant living end **5a** was end-capped in situ with excess sodiomalonic ester. Figure 2 shows the MWDs of the polymers thus prepared as a function of the monomer-to-initiator ratio $[IBVE]_0/[\mathbf{2a}]_0$.

Irrespective of polymerization temperature and the $[IBVE]_0/[\mathbf{2a}]_0$ ratio, all the polymers possessed very narrow MWDs, and the molecular weight increased in

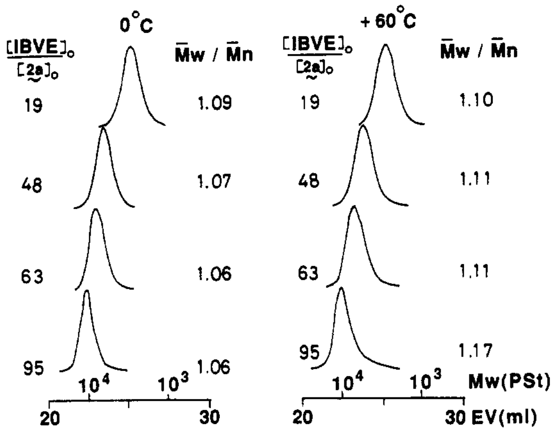


Figure 2. MWD of acetoxy/malonate heterotelechelic polymers (**3a**); polymerization by **2a**/$EtAlCl_2$ in *n*-hexane at 0 °C (A) and +60 °C (B): $[IBVE]_0 = 0.76$ M; $[\mathbf{2a}]_0 = 8$–40 mM; [1,4-dioxane] = 1.2 M; $[EtAlCl_2]_0/[\mathbf{2a}]_0 = 1.0$ (0 °C) or 0.80 (+60 °C); conversion ~100%.

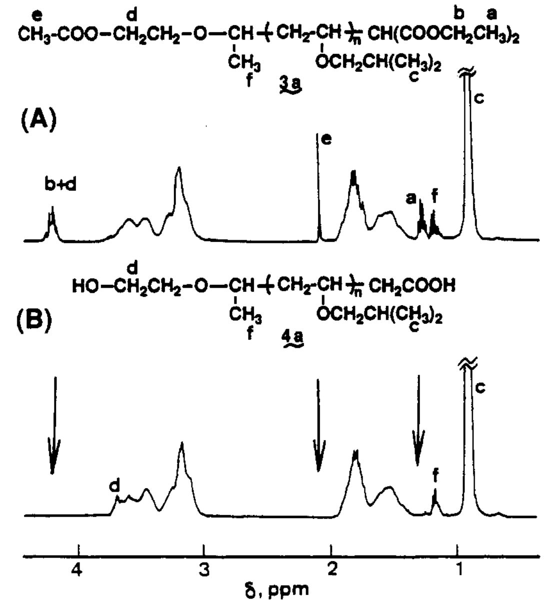


Figure 3. ¹H NMR spectra ($CDCl_3$) of heterotelechelic polymers: (A) polymer **3a** obtained at +60 °C (acetoxy/malonate; entry 5, Table II) and (B) polymer **4a** (hydroxy/carboxy; from sample A).

direct proportion to the monomer-to-initiator feed ratio. Thus, living polymerization proved operatable even at +60 °C with initiator **2a**, which carries a polar ester group.

A typical ¹H NMR spectrum of the end-capped polymer obtained at +60 °C is given in Figure 3A. Consistent with the expected telechelic structure **3a**, all key absorptions of the poly(IBVE) main chain (e.g., peak c), the α-end acetate (peaks d and e), and the ω-end malonate (peaks a and b) were seen, and absorptions indicative of byproducts were absent. The $\overline{DP}_n$(obd) of **3a** was determined from the peak intensity ratio of the main chain (peak c) to the terminal malonate (peak e) (Table II). The observed $\overline{DP}_n$ was in good agreement with the calculated value ($[IBVE]_0/[\mathbf{2a}]_0$) based on the assumption that one molecule of **2a** produces one polymer. The determination of $\overline{DP}_n$ by 270 MHz ¹H NMR is applicable to **3a** and other polymers with $\overline{DP}_n$ up to 100 (estimated error, ±10%).

Based on the fact that $[\text{living end}]_0 = [\text{initiator } \mathbf{2}]_0$, the end functionality was determined from the ratio [end group]/$[\mathbf{2a}]_0$ for both α-end acetate ($\bar{F}_n(\alpha)$) and ω-end malonate ($\bar{F}_n(\omega)$). The acetate content $[CH_3COO]$(mol/L) was obtained from the NMR intensity ratio of the acetate methyl (peak e) to the poly(IBVE) pendant methyl (peak c). Similarly, the terminal malonate content was given by the ratio of peak b to c; because of the overlapping of peaks b and d, the integral of peak b was determined by subtracting the contribution of peak d, which was obtained from the integral of another α-end signal e, from the observed integral b + d. Table II (entries 1–8) shows the $\bar{F}_n(\alpha)$ and $\bar{F}_n(\omega)$ values thus obtained for a series of polymer **3a** samples. Despite that these functionality values were based on the NMR signal ratios that are independent of each other, they are invariably very close to unity and thereby demonstrate the attachment of both one acetate and one malonate functions per polymer even for the samples produced at +60 °C and with $\overline{DP}_n$ up to 100.

As shown in Figure 3B, both acetoxy and malonate terminals of **3a** could readily be transformed into the corresponding hydroxy and carboxy terminals (**4a**), respectively, by the standard alkaline hydrolysis, followed by thermal decarboxylation (eq 1).[8] The signals associated

$$\underset{\mathbf{3a}}{CH_3COO\sim\sim CH(COOC_2H_5)_2} \xrightarrow[2)\ H^+/\Delta]{1)\ OH^-} \underset{\mathbf{4a}}{HO\sim\sim COOH} \quad (1)$$

with the acetate (peaks d and e) and the malonate (peaks a and b) terminals are absent for the hydrolysis product. Polymer **4a** is the first example of heterotelechelic poly(vinyl ether) with hydroxy and carboxy terminals, which may undergo condensation reactions with each other.

(c) Synthesis of NH_2/COOH Heterotelechelic Poly(IBVE) (4b). In a manner similar to the synthesis of **4a**, amino- and carboxy-capped heterotelechelic poly(IBVE) **4b** was prepared (Scheme I and eq 2). For this, we

$$\underset{\mathbf{3b}}{[(CH_3)_3COOC]_2N\sim\sim CH(COOC_2H_5)_2} \xrightarrow[2)\ H^+/\Delta\ 3)\ H^+]{1)\ OH^-} \underset{\mathbf{4b}}{H_2N\sim\sim COOH} \quad (2)$$

employed a new initiator **2b** that carries a bis(*tert*-butoxycarbonyl)imido function,[4] which turned out better suited to our purpose than the phthalimide counterpart previously employed,[16] and IBVE was polymerized with the **2b**/$EtAlCl_2$ system in *n*-hexane containing 1,4-dioxane at 0 and +60 °C. The resulting living end (**5b**)[16] was then end-capped with sodiomalonic ester to give heterotelechelic precursor polymer **3b**.

Structural analysis of the products by ¹H NMR spectroscopy confirmed the structure expected for **3b** (Figure 4A). For example, the spectrum clearly showed signals assigned to the imido's methyl (α-end; the sharp singlet d) and the malonate's ethyl groups (ω-end; peaks a and b). The end functionality $\bar{F}_n(\alpha)$ (terminal imido/polymer) was determined from the intensity ratio of peak d to peak c and the initial concentration of initiator **2b**, (= [living end]). Because of the overlapping of peak d and adjacent peaks, the integral of peak d was determined by subtracting the contribution of adjacent peaks. $\bar{F}_n(\omega)$ (terminal malonate/polymer) was determined as already discussed for **3a** (see above); and their values are listed in Table II. For the sample obtained at 0 °C (entry 9), both $\bar{F}_n(\alpha)$ and $\bar{F}_n(\omega)$ were close to unity, indicating the attachment of one imido and one malonate groups per polymer. For the synthesis at +60 °C (entry 10), on the other hand, clearly lower $\bar{F}_n(\alpha)$ and $\bar{F}_n(\omega)$ values (~0.6) were obtained, and $\overline{DP}_n$(obd) value was higher than the calculated value. The terminal imido and malonate groups of **3b** could readily be converted into an amino and a carboxy function, respectively, to give heterotelechelic polymer **4b** (eq 2). The end-groups transformation consisted of alkaline hy-

Table II
Synthesis of Telechelic Poly(IBVE) (3) via End-Capping with $NaCH(COOC_2H_5)_2$ or LiC_6H_5[a]

entry	initiator	functional group α-end	 ω-end	T, °C	t, min	$\overline{DP}_n$ (calcd)	$\overline{DP}_n$ (obsd)	$\bar{M}_w/\bar{M}_n$	$\bar{F}_n(\alpha)$[c]	$\bar{F}_n(\omega)$[c]
1	**2a**	$OCOCH_3$	$CH(COOC_2H_5)_2$	0	15	19	17	1.09	1.10	1.09
2				0	90	48	43	1.07	1.08	1.10
3				0	300	63	59	1.06	1.09	1.07
4				0	21 h	95	88	1.06	1.05	1.08
5				+60	1	19	19	1.10	1.02	1.03
6				+60	3	48	47	1.11	1.04	1.01
7				+60	6	63	60	1.11	1.06	1.06
8				+60	10	95	91	1.17	1.03	1.04
9	**2b**	$N[COOC(CH_3)_3]_2$	$CH(COOC_2H_5)_2$	0	10	10	10	1.18	0.95	0.96
10				+60	0.5	10	16	1.30	0.60	0.61
11	**2c**	$CH(COOC_2H_5)_2$	$CH(COOC_2H_5)_2$	0	15	19	18	1.08		2.18
12				+60	1	19	19	1.16		2.04
13[b]	**2c**	$CH(COOC_2H_5)_2$	C_6H_5	0	15	19	18	1.08	1.03	1.02
14[b]				+60	1	19	19	1.10	1.02	1.01

[a] $[IBVE]_0$ = 0.76 M (10 vol %); $[\mathbf{2}]_0$ = 7.0–76.0 mM; $[EtAlCl_2]_0/[\mathbf{2}]_0$ = 2.0 (for entries 9 and 10); for other samples, $[EtAlCl_2]_0/[\mathbf{2}]_0$ = 1.0 (0 °C) or 0.80 (+60 °C); [1,4-dioxane] = 1.2 M (10 vol %); conversion ~ 100%. Living polymers were quenched with sodiomalonic ester except for entries 13 and 14. [End-capping agent]/$[\mathbf{2}]_0$ = 10. For all runs, the reaction of the capping agent with the living end was for 60 min. [b] Terminated with phenyllithium. [c] Determined by ^1H NMR with an estimated error ±10%; see text for details.

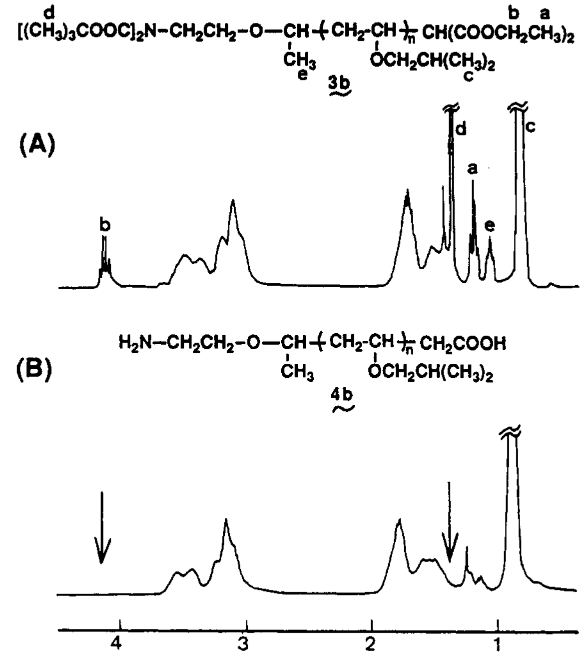


Figure 4. ^1H NMR spectra ($CDCl_3$) of heterotelechelic polymers: (A) polymer **3b** obtained at 0 °C (imido/malonate; entry 9, Table II) and (B) polymer **4b** (amino/carboxy; from sample A).

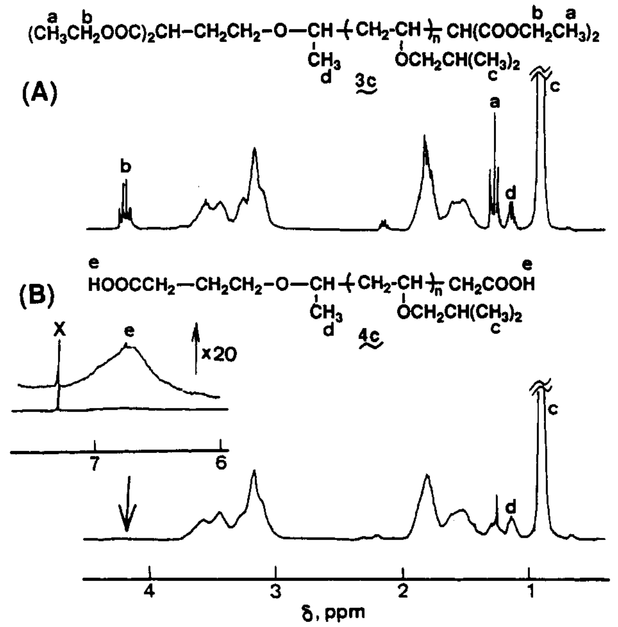


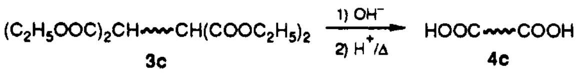
Figure 5. ^1H NMR spectra ($CDCl_3$) of homotelechelic polymers: (A) polymer **3c** obtained at +60 °C (malonate; entry 12, Table II) and (B) polymer **4c** (carboxy; from sample A). The cross (X) indicates the signal due to $CHCl_3$.

drolysis/thermal decarboxylation on the malonate and subsequent acidolysis of the (butoxycarbonyl)imido (with 6 N HCl).[4] Figure 4B illustrates a typical ^1H NMR spectrum of the product, which shows the complete absence of the precursor terminals (peaks a, b, and d in Figure 4A).

(d) Synthesis of COOH/COOH Telechelic Poly(IBVE) (4c). In addition to the OH/COOH (**4a**) and the NH_2/COOH (**4b**) heterotelechelic polymers, the COOH/COOH homotelechelic counterpart (**4c**) can also be prepared by our method (Scheme I and eq 3). Although the same polymer has already been prepared at temperatures below 0 °C on the basis of the HI/I_2 initiating system,[9] the use of the malonate-carrying initiator **2c** with $EtAlCl_2$ and 1,4-dioxane now permitted the synthesis to be operable well above room temperature, where the base-stabilized living species **5c** can survive.

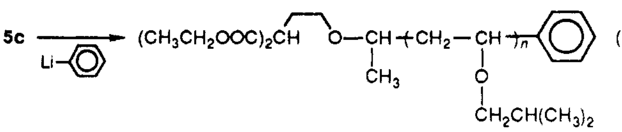
The ^1H NMR spectrum of the malonate-quenched polymer obtained even at +60 °C (Figure 5A) was fully consistent with the structure **3c**, as evidenced by absorptions a and b due to the α-end and ω-end malonates along with the α-end methyl signal d. $\bar{F}_n(\omega)$ was determined by comparing the concentration of the malonate groups (the intensity ratio of peak b to c) with the initial concentration of initiator **2c**. As shown in Table II (entries 11 and 12), the polymers, either obtained at 0 or +60 °C, exhibited very narrow MWDs ($\bar{M}_w/\bar{M}_n$ < 1.1) and $\bar{F}_n(\omega)$ values close to two. Accordingly, $\overline{DP}_n$(obsd) values were in good agreement with the calculated values, indicating the formation of telechelic malonate-capped poly(IBVE) (**3c**) that has exactly two malonate groups per chain.

As already shown,[8] the conversion of the terminal malonates into two carboxy groups by hydrolysis/decarboxylation (eq 3) proceeded smoothly (Figure 5B). No difference was found between the samples of the biscarboxylate polymer **4c** obtained with the **2c**/$EtAlCl_2$/dioxane and the HI/I_2[8] systems.



$$\underset{\mathbf{3c}}{(C_2H_5OOC)_2CH\sim\sim CH(COOC_2H_5)_2} \xrightarrow[2)\ H^+/\Delta]{1)\ OH^-} \underset{\mathbf{4c}}{HOOC\sim\sim COOH} \tag{3}$$

3. Synthesis of Heterotelechelic Poly(IBVE) with Phenyl Terminal (8). On the basis of the search for end-capping agents shown in Table I, terminal functionalization was also examined with use of the phenyl carbanion (LiC_6H_5) in place of the malonate anion. Thus, as typical examples, IBVE living polymers **5c** were generated by the malonate type initiator **2c** along with $EtAlCl_2$ and 1,4-dioxane in *n*-hexane at 0 and +60 °C, and subsequently end-capped with phenyllithium to give a phenyl-capped polymer 8 (eq 4). This phenyl end-capping method is



(4)

8

equally applicable to the living poly(IBVE) initiated with the other **2**/$EtAlCl_2$ systems. According to the conversion analysis by gas chromatography, the polymerization was terminated immediately after the addition of the lithium salt.

Structural analysis by ^1H NMR spectroscopy (Figure 6) confirmed the formation of malonate/phenyl heterotelechelic polymer 8, as evidenced by the signals of the α-end malonate group (peaks a and b) and the ω-end phenyl group (peak e), along with the poly(IBVE) main-chain signals (peak c, etc.). $\bar{F}_n(\alpha)$ was determined from the concentration of the malonate group (the intensity ratio b/c), and $\bar{F}_n(\omega)$ from the concentration of the phenyl group (intensity ratio e/c), both compared with $[\mathbf{2d}]_0$. $\overline{DP}_n$(obsd) was determined from the peak intensity ratio of the main-chain protons (peak c) to the malonate protons (peak b). Table II shows that the polymers, obtained at either 0 or +60 °C, possess a very narrow MWD, $\bar{F}_n(\alpha)$ and $\bar{F}_n(\omega)$ close to unity, and $\overline{DP}_n$(obsd) value in good agreement with the calculated value ($[IBVE]_0/[\mathbf{2d}]_0$). All these data corroborate the quantitative attachment of one malonate and one phenyl group per polymer. The malonate terminal can be converted into the acid form without deteriorating the phenyl end group. The terminal phenyl moiety would prove useful as a versatile site for attaching functional groups via Friedel–Crafts and other reactions.

Experimental Section

Preparation of Functionalized Vinyl Ethers (1). 2-Acetoxyethyl vinyl ether (**1a**)[17] and diethyl 2-(vinyloxy)ethyl malonate (**1c**)[8] were prepared according to the literature methods.

Di-*tert*-butyl [*N*-[2-(vinyloxy)ethyl]imido]dicarboxylate (**1b**) was prepared as follows. In a 300-mL, three-necked, round-bottom flask fitted with a magnetic stirrer, a reflux condenser, and a dropping funnel were charged di-*tert*-butyl iminodicarboxylate, $HN[CO_2C(CH_3)_3]_2$ (10.0 g, 46 mmol)(Aldrich, purity 95%), sodium hydroxide aqueous solution (1 M, 43 mL, 43 mmoL NaOH), and dimethyl sulfoxide (100 mL). After stirring for 1 h at room temperature, the reaction mixture was then warmed to 80 °C in an oil bath, and 2-chloroethyl vinyl ether (9.2 g, 92 mmoL) and tetra-*n*-butylammonium bromide (1 g; a phase-transfer catalyst) were added. The heterogeneous solution was stirred at this temperature for 6 h, cooled to room temperature, and then poured into 500 mL of water. The aqueous phase was extracted with three 50-mL portions of diethyl ether, and the ether extracts were combined with the organic layer. The combined organic phase was washed twice with water (100 mL each) and evaporated under reduced pressure to give a yellowish viscous liquid. The crude product was purified by preparative size-exclusion chromatography (column, Shodex 2001 polystyrene gel; solvent, $CHCl_3$); the collected fractions in chloroform were dried with sodium sulfate overnight and evaporated to dryness under reduced pressure to give **1b** as a light yellowish viscous liquid: yield, 60%; purity >98% by ^1H NMR. ^1H NMR ($CDCl_3$): δ 6.44 (q, 1 H, =CH—), 4.11 (m, 2 H, CH_2=), 3.86 (t, 4 H, —CH_2CH_2—), 1.50 (s, 18 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 152.4 (C=O), 151.4 (=CH), 86.7 (CH_2=), 82.2 (—C—), 66.0 (OCH_2), 44.9 (CH_2N), 27.9 (CH_3).

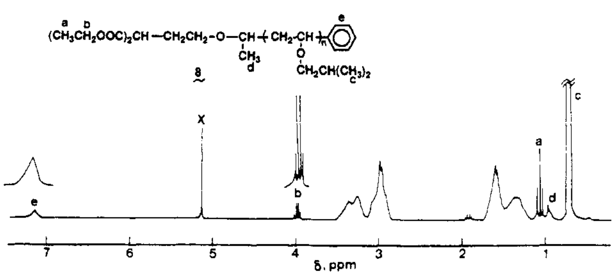


Figure 6. ^1H NMR spectrum (CD_2Cl_2) of malonate/phenyl heterotelechelic poly(IBVE) 8 obtained at +60 °C (entry 14, Table II). The cross (X) indicates the peak due to CH_2Cl_2.

Initiators (2). Functionalized initiators (**2a–d**) were prepared from trifluoroacetic acid and the corresponding vinyl ethers (1) as reported.[5]

Capping Agents. Diethyl sodiomalonate (200 mM in 1,4-dioxane) was prepared as reported.[8] Acetaldehyde 3-lithiopropyl ethyl acetal (**6**) and (2-lithioethoxy)trimethylsilane (**7**) were synthesized by lithiating the corresponding bromides according to the method of Dias and McCarthy.[10] *n*-Butyllithium (1.6 M in tetrahydrofuran), and phenyllithium [1.8 M in a cyclohexane–ether (70/30, v/v) mixture] were of commercial source (Aldrich) and were used under dry nitrogen without further purification.

Other Materials. IBVE and ethyl vinyl ether (**1d**), *n*-hexane (polymerization solvent), 1,4-dioxane (added base), and *n*-heptane (internal standard for gas chromatography) were purified by the usual methods[7,13] and distilled twice over calcium hydride just before use. Commercial $EtAlCl_2$ (Kanto Chemicals; 1.0 M in *n*-hexane) and CF_3COOH (Wako Chemicals; >99%) were used under dry nitrogen without further purification.

Procedures. Polymerization was performed under dry nitrogen in baked glass tubes each equipped with a three-way stopcock. The reactions were initiated by sequential addition of the initiator **2** and $EtAlCl_2$ solutions (0.50 mL each) into a monomer solution (4.0 mL in *n*-hexane) containing 1,4-dioxane (0.50 mL, 1.2 M, 10 vol %) at 0 or +60 °C. The resulting living polymers were terminated with solutions of a capping agent (see Table I), which was 10-fold molar excess over the initiator (**2**). The recovery and purification of the polymers were done as described already.[4,5]

Deprotection. Regardless of the α-end function X, the malonate-capped poly(IBVE) (**3a–c**) (100 mg) was dissolved in ethanol (10 mL), and hydrolysis/decarboxylation was carried out as reported.[8] For X = $OCOCH_3$ (**3a**) and $CH(COOC_2H_5)_2$ (**3c**), the hydrolysis/decarboxylation led to the fully deprotected telechelic polymers, **4a** (OH/COOH) and **4c** (COOH/COOH). For X = $N[COOC(CH_3)_3]_2$ (**3b**), the decarboxylation product was dissolved in nitromethane (20 mL) and treated with 6 N hydrochloric acid (50-fold molar excess over the imide function in the polymer) for 6 h at room temperature with stirring. The reaction mixture was washed sequentially with an NaOH aqueous solution (equivalent to the hydrochloric acid employed) and water, isolated by evaporation, and finally dried in vacuo to give **4b** (NH_2/COOH terminals).

Polymer Characterization. The MWD of the polymers was measured by size-exclusion chromatography in chloroform at room temperature on JASCO Trirotor chromatograph equipped with three polystyrene gel columns (Shodex; exclusion limits were K-802, 5×10^3; K-803, 7×10^4; K-804, 4×10^5) that were calibrated against 12 standard polystyrene samples. The $\bar{M}_w/\bar{M}_n$ of the polymers were calculated from size-exclusion eluograms. ^1H NMR spectra were recorded at 270 MHz in $CDCl_3$ at room temperature on a JEOL GSX-270 spectrometer. $\overline{DP}_n$ was determined by ^1H NMR end-group analysis (see Results and Discussion section).

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References and Notes

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Registry No. 1b, 137257-50-2; HN[$CO_2C(CH_3)_3$]$_2$, 51779-32-9; Cl(CH_2)$_2$OCH=CH_2, 110-75-8; EtAlCl$_2$, 563-43-9; 1,4-dioxane, 123-91-1.