Polymer Bulletin 21, 357–363 (1989)

Polymer Bulletin

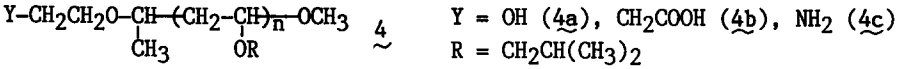
Synthesis of end-functionalized polymers by living cationic polymerization of isobutyl vinyl ether with $EtAlCl_2$

Hajime Shohi*, Mitsuo Sawamoto, and Toshinobu Higashimura**

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto, 606 Japan

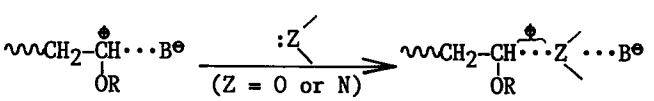
SUMMARY

A series of end-functionalized polymers (4), carrying a hydroxyl, carboxyl, or primary amino terminal group Y, were obtained by living cationic polymerization of isobutyl vinyl ether. The initiating systems of choice consisted of $EtAlCl_2$ and the trifluoroacetate [2; $X\text{-}CH_2CH_2OCH(CH_3)OOCCF_3$; X = $OOCCH_3$, $CH(COOC_2H_5)_2$, $N(COOC(CH_3)_3)_2$] obtained from a vinyl ether with a protected functional pendant group. In the presence of 1,4-dioxane, the 2/$EtAlCl_2$ systems invariably induced a well-defined living polymerization of isobutyl vinyl ether in *n*-hexane at 0 to +40°C to give polymers, the α-end group (X) of which was derived from the initiator 2. Subsequent deprotection of X of these polymers led to 4, all of which were shown to have a very narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.07–1.18), a number-average molecular weight ($\bar{M}_n$ = 10^3–10^4) controllable by the monomer/2 molar feed ratio, and one terminal function Y per chain.



INTRODUCTION

Living cationic polymerization of vinyl ethers has been shown to occur with ethylaluminum dichloride ($EtAlCl_2$) in the presence of an externally added weak base (1), including an ester (2) and ether (3). The added base is proposed to stabilize the otherwise unstable growing carbocation by cationic charge delocalization through a strong nucleophilic interaction, as shown in Scheme I where $B^{\ominus}$ is the counteranion derived from $EtAlCl_2$.

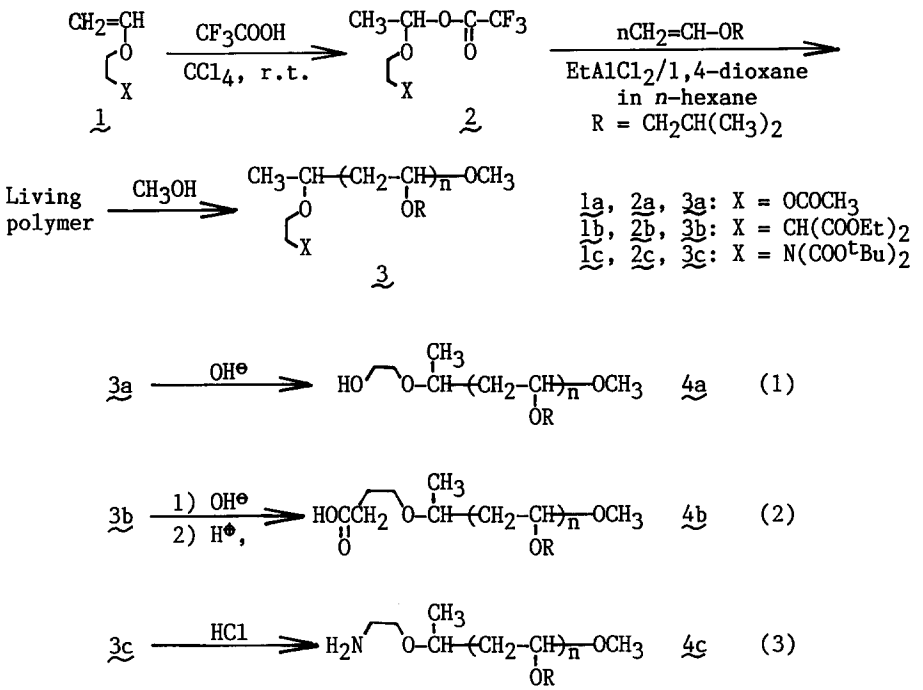


Scheme I. Carbocation stabilization by an added base.

In addition of an added base, the $EtAlCl_2$-mediated living polymerization usually employs a cationogen (or initiator), typically an acetate CH_3COOR, that generates an initiating cation ($R^{\oplus}$) with aid of the organoaluminum (2). We have shown the formation of one living chain per molecule of the cationogen, which fact in turn implies the attachment of the initiator fragment R to each polymer terminal. It readily follows (Scheme II) that the use of similar but functionalized initiators 2, obtained from a vinyl

*Permanent address: Polymer Research Laboratory, Cooperate Research Institute, Sekisui Chemical Company, Ltd., 2-1 Hyaku Yama, Shimamoto-cho, Mishima-gun, Osaka 618, Japan

**To whom offprint requests should be sent



Scheme II. Synthesis of end-functionalized polymers 4 with $EtAlCl_2$.

ether 1, will lead to polymers 3 with a terminal function X. The object of this study was to synthesize end-functionalized poly(vinyl ethers) 4 in a controlled manner on the basis of this methodology.

The synthesis route illustrated in Scheme II is similar to our previous method (4-6) using a hydrogen iodide adduct of a functionalized vinyl ether as an initiator and iodine as an activator, in that the terminal functionality is derived from the initiator. However, the use of the 2/$EtAlCl_2$ is unpreceded in concept, because the living polymerization initiated by this system is based on the carbocation stabilization by an added base (Scheme I), whereas that with the hydrogen iodide adduct utilizes the nucleophilic iodide counteranion for stabilizing the growing center (1).

We herein report the synthesis of a series of end-functionalized polymers 4 carrying a terminal hydroxyl (4a), carboxyl (4b), or primary amino (4c) group, according to Scheme II that consists of the living cationic polymerization of isobutyl vinyl ether (IBVE) initiated by the 2/$EtAlCl_2$ system in *n*-hexane in the presence of 1,4-dioxane as an added base, followed by deprotection of the terminal group X of the precursor polymer 3 (Eq. 1-3).

RESULTS AND DISCUSSION

Synthesis of Trifluoroacetate Initiator 2

Despite our frequent use of vinyl ether-acetic acid adducts as the initiators for the living polymerization with $EtAlCl_2$ and an added base (1), we decided in this study to replace them with the corresponding trifluoroacetates (2). It turned out that the reaction of the functionalized

TABLE I
Synthesis of Polymer 3 by the Living Cationic Polymerization of IBVE with 2/$EtAlCl_2$ in *n*-Hexane in the Presence of 1,4-Dioxane[a]

Entry	X	$[EtAlCl_2]_0/[2]_0$	Temp, °C	$\overline{DP}_n$[b] (calcd)	$\overline{DP}_n$[c,d] (obd)	$\bar{M}_w/\bar{M}_n$[e]	$\bar{F}_n(A)$[d,f]	$\bar{F}_n(B)$[d,g]
1	$OOCCH_3$	1.0	0	19.0	18.0	1.07	1.06	1.00
2	"	0.50	+40	19.0	19.1	1.13	1.02	1.02
3	$CH(COOEt)_2$	0.80	0	14.7	14.5	1.14	1.02	1.01
4	"	0.50	+40	19.0	20.2	1.18	1.09	1.03
5	$N(COO^tBu)_2$	4.0	0	10.0	9.9	1.13	0.96	0.95

a) $[IBVE]_0$ = 0.38 M (5.0 vol %); $[2]_0$ = 20 - 40 mM; [1,4-dioxane] = 1.2 M (10 vol %); conversion ca. 100%, by gas chromatography.
b) $\overline{DP}_n(calcd) = [IBVE]_0/[2]_0$.
c) $\overline{DP}_n(obd) = [IBVE]_0/[P^*]$; [P*] represents the living end concentration determined from the peak intensity of the acetal terminal; see text.
d) Measured by ^1H NMR (90 MHz, in $CDCl_3$).
e) Measured by size-exclusion chromatography in $CHCl_3$ at room temperature with a polystyrene calibration.
f) $\bar{F}_n(A) = [X]/[2]_0$; [X] represents the concentration of the terminal functional group X derived from 2; see text.
g) $\bar{F}_n(B) = [X]/[P^*]$.

vinyl ethers 1 into 2 is invariably quantitative with trifluoroacetic acid but not with acetic acid; in contrast, the addition of acetic acid to nonpolar alkyl vinyl ethers is quantitative. Thus, the trifluoroacetate initiators 2 were prepared by mixing 1 with an equimolar amount of CF_3COOH in CCl_4 at room temperature under dry nitrogen (7). After its quantitative formation had been confirmed by ^1H and ^{13}C NMR spectroscopy, the resulting solution of 2 was directly employed for the subsequent living polymerization of IBVE.

Hydroxy-Capped Polymer 4a

IBVE was polymerized at 0 and +40°C in *n*-hexane containing 1,4-dioxane (1.2 M; 10 vol %) with $EtAlCl_2$ in conjunction with trifluoroacetate 2a, which carries an acetate pendant group as a protected form of a hydroxyl function. The $EtAlCl_2$/2a feed ratio was set in the range 0.50 - 1.0, on the basis of preliminary experiments carried out at various $EtAlCl_2$ concentrations (8). As summarized in Table I (entry 1 and 2), the polymerization quantitatively gave living polymers with very narrow molecular weight distributions (MWD) ($\bar{M}_w/\bar{M}_n \leq 1.1$).

Figure 1A shows the ^1H NMR spectrum of a typical product (sample 1, Table I), along with peak assignment. All key absorptions of the poly(IBVE) main-chain (a, b, c, f, and g) and the initiator fragment (α-end; h, k, and l) are seen, all of which are consistent with the expected structure of polymer 3a. The additional signals d and e are due to the acetal terminal [ω-end; $-CH_2\underline{CH}(iBu)O\underline{CH_3}$] that arises from quenching the living end with ammoniacal methanol (4).

Comparison of the integrated intensities of these key resonances confirmed the clean and quantitative formation of 3a (Table I). For example, the concentration ([X]) of the α-end group X, determined from peak k or l and peak a [CH_3 of the poly(IBVE) chain], was shown to be equal to the initial concentration of the initiator 2a ($\bar{F}_n(A) = [X]/[2a]_0 = 1$). [X] was also found equal to the living end concentration [P*] based on the acetal

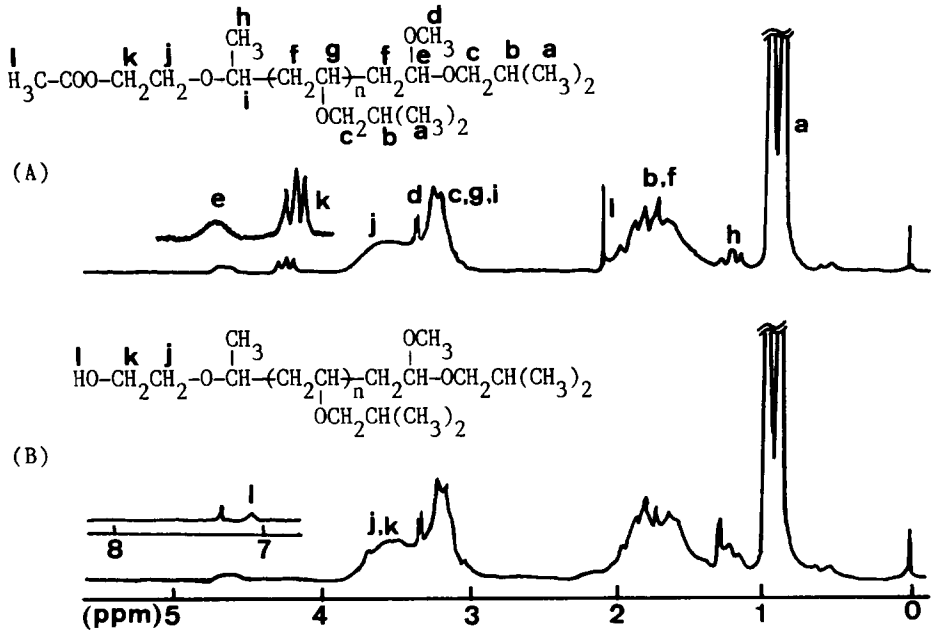


Figure 1. ^1H NMR spectra (90 MHz, $CDCl_3$):
(A) acetate-capped poly(IBVE) 3a (sample 1, Table I);
(B) hydroxy-capped poly(IBVE) 4a obtained from sample 1.

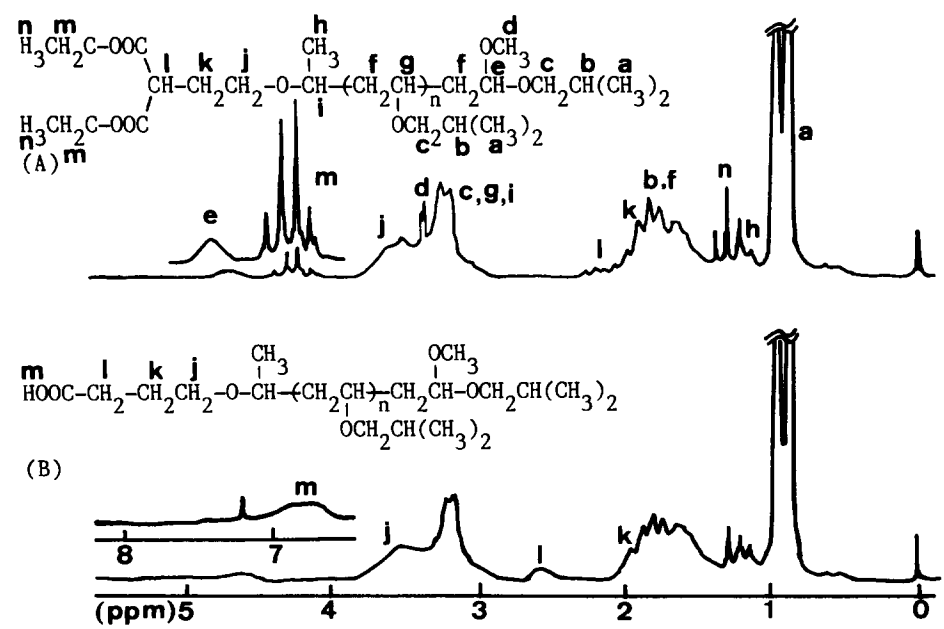


Figure 2. ^1H NMR spectra (90 MHz, $CDCl_3$):
(A) malonate-capped poly(IBVE) 3b (sample 3, Table I);
(B) carboxy-capped poly(IBVE) 4b obtained from sample 3.

terminal e ($\bar{F}_n$(B) = [X]/[P*] = 1); i.e., the signal intensity ratio of e/k was very close to the expected value (1/2). In addition, the number-average degree of polymerization, $\overline{DP}_n$(obsd), which was determined from the ratio of the main-chain and living end protons (a/e), was in agreement with the calculated value ($\overline{DP}_n$(calcd) = $[IBVE]_0/[2a]_0$).

All these data show the IBVE polymerization by 2a/$EtAlCl_2$ in the presence of 1,4-dioxane to produce well-defined polymer 3a which has one terminal function X per chain and a controlled molecular weight. It should be emphasized that the synthesis operates even at +40°C, at which temperature the corresponding process using the hydrogen iodide adduct has not proved successful yet (4-6).

The terminal acetate group of 3a was turned out to be readily converted into a hydroxyl function (4a) by the standard alkaline hydrolysis in ethanol at room temperature (Eq. 1, Scheme II) (6,9); a typical example of the ^1H NMR spectrum of the hydrolysis product is given in Figure 1B. The signals associated with the acetate terminal of 3a (peaks k and l, Figure 1A) are absent in Figure 1B, where the alcoholic proton of 4a is in turn seen around δ 7.1 ppm.

Carboxy-Capped Polymer 4b

In a fashion similar to the above, the carboxyl version 4b was prepared from vinyl ether 1b via the precursor 3b (Scheme II). Thus, the polymerization of IBVE by the 2b/$EtAlCl_2$ system was carried out in *n*-hexane in the presence of 1,4-dioxane, which again gave living polymers of narrow MWDs in quantitative yield both at 0 and +40 °C (Table I, entry 3 and 4). The ^1H NMR spectum of the product (Figure 2A) is fully consistent with the structure 3b, as evidenced by signals h, k, m, and n for the malonate group and d and e for the acetal terminal. Quantitative attachment of the malonate function to the polymer's α-end was shown by comparing the peak intensity ratios (see Table I); $\overline{DP}_n$(obsd) of 3b also proved controllable by the IBVE/2b molar feed ratio.

As shown in Figure 2B, the malonate terminal of 3b could readily be transformed into the corresponding carboxylic acid (4b) by alkaline hydrolysis in ethanol at room temperature, followed by thermal decarboxylation in 1,4-dioxane at 90°C (Eq. 2, Scheme II) (6). The quantiative deprotection is shown, for example, by the complete disappearance of the ester's ethyl groups (peaks m and n; cf. Figure 2A), coupled with the observation of the acid proton as a broad signal m in Figure 2B.

Amine-Capped Polymer 4c

In our previous study (10), we have successfully employed 2-(vinyloxy)ethylphthalimide, as a vinyl ether with a protected amino group, for living cationic polymerization. It soon turned out, however, that the reaction of this monomer with CF_3COOH does not quantitatively proceed in CCl_4 at room temperature. Thus, we newly synthesized *N*-[2-(vinyloxy)ethyl]di-*t*-butylcarboxyimide (1c), another protected form of an amino-functionalized vinyl ether, for which addition of CF_3COOH now proved quantitative under the same conditions to give 2c (8).

In the presence of $EtAlCl_2$ and 1,4-dioxane, the initiator 2c induced living polymerization of IBVE in *n*-hexane at 0°C to form polymers (3c) with a narrow MWD and a controlled molecular weight (Table I, entry 5). The ^1H NMR spectrum of the product (Figure 3A) clearly showed the quantitative incorporation of the imide function of 2c into the polymer terminal (e.g., peak l for the *t*-butyl moiety). This signal, though very sharp, could not fully be resolved from the broad absorption appearing around δ 1.3-2.1 ppm, so that the concentration of the imide function was determined by comparing the intensity ratio of the latter broad band (including peak l) to another

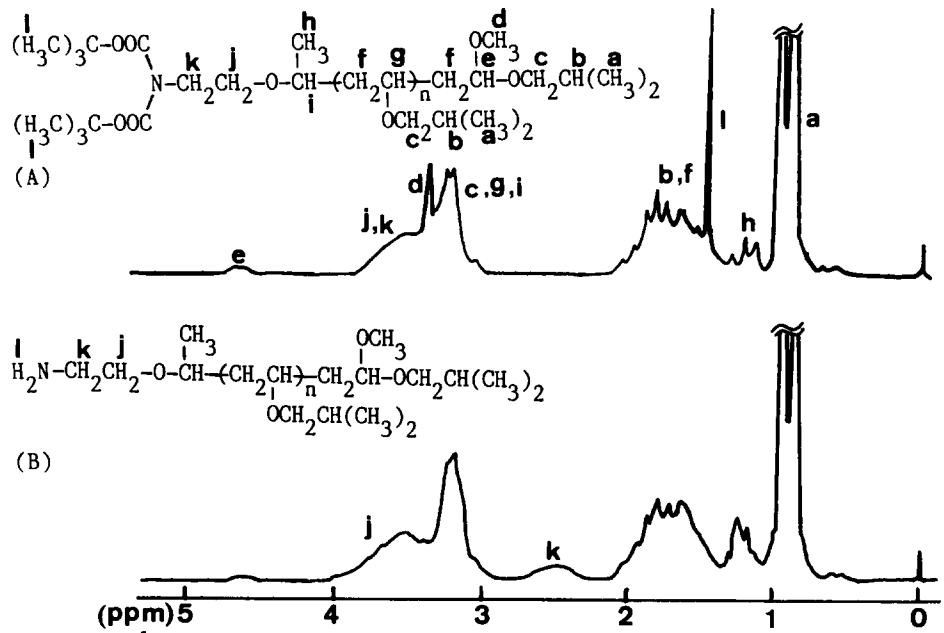


Figure 3. ^{1}H NMR spectra (90 MHz, $CDCl_3$):
(A) imide-capped polym(IBVE) 3c (sample 5, Table I);
(B) amine-capped poly(IBVE) 4c obtained from sample 5.

broad absorption in the range δ 3-4 ppm.

Deprotection of the imide group in the precursor 3c was carried out in nitromethane at room temperature in the presence of a few drops of concentrated hydrochloric acid (Eq. 3, Scheme II) (11). ^{1}H NMR analysis of the product (Figure 3B) again showed quantitative conversion of the imide group into a primary amino function (or polymer 4c). For example, the imide's sharp signal 1 (cf. Figure 3A) is now completely absent, whereas the methylene protons adjacent to the primary amino group are seen as a broad signal around δ 2.5 ppm.

In conclusion, the synthesis of end-functionalized poly(IBVE) 4 has been shown to be feasible, not only via the living cationic polymerization by the hydrogen iodide-based initiating system (based on the carbocation stabilization with a nucleophilic counteranion) (4-6) but also via the similar process by the 2/$EtAlCl_2$ system (via the carbocation stabilization with an added base; Scheme II), where the latter is advantageous in that it operates even above room temperature. The living polymerization using the trifluoroacetate 2 is currently studied in detail and to be the subject of our future publication (8).

EXPERIMENTAL

The monomer (IBVE), solvent (*n*-hexane), 1,4-dioxane, and $EtAlCl_2$ were purified as reported (2,3). Polymerization by 2/$EtAlCl_2$ was carried out under dry nitrogen in a baked glass tube equipped with a three-way stopcock. The reaction was initiated by sequential addition of solutions of 2 and $EtAlCl_2$ into a mixture of IBVE and 1,4-dioxane in *n*-hexane, and quenched with ammoniacal methanol. The procedures for the sytheses of polymer 4 and vinyl ether 1c will be reported in detail elsewhere (8).

REFERENCES

(1) For a review, T. Higashimura, S. Aoshima, and M. Sawamoto, Makromol. Chem., Macromol. Symp., 13/14, 457 (1988).
(2) S. Aoshima and T. Higashimura, Polym. Bull., 15, 417 (1986).
(3) T. Higashimura, Y. Kishimoto, and S. Aoshima, Polym. Bull., 18, 111 (1987).
(4) For a review, M. Sawamoto, S. Aoshima, and T. Higashimura, Makromol. Chem., Macromol. Symp., 13/14, 513 (1988).
(5) S. Aoshima, K. Ebara, and T. Higashimura, Polym. Bull., 14, 425 (1985).
(6) M. Sawamoto, T. Enoki, and T. Higashimura, Macromolecules, 20, 1 (1987).
(7) R. R. Gallucci and R. C. Going, J. Org. Chem., 47, 3517 (1982).
(8) H. Shohi, M. Sawamoto, and T. Higashimura, Macromolecules, to be published.
(9) S. Aoshima, T. Nakamura, N. Uesugi, M. Sawamoto, and T. Higashimura, Macromolecules, 18, 2097 (1985).
(10) T. Hashimoto, H. Ibuki, M. Sawamoto, and T. Higashimura, J. Polym. Sci., Part A, Polym. Chem., 26, 3361 (1988).
(11) L. A. Carpino, J. Org. Chem., 29, 2820 (1964).

Accepted March 4, 1989 S