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Living Cationic Polymerization of Vinyl Monomers by Organoaluminum Halides. 3. Living Polymerization of Isobutyl Vinyl Ether by $EtAlCl_2$ in the Presence of Ester Additives

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ABSTRACT: Three carboxylate esters ($R-COOC_2H_5$; R = CH_3, C_6H_5, OC_2H_5), added in excess to the reaction mixtures, have permitted living cationic polymerization of isobutyl vinyl ether (IBVE) initiated by the IBVE–acetic acid adduct [$CH_3CH(O\textit{i}Bu)OCOCH_3$ (1)]/$EtAlCl_2$ system in *n*-hexane at 0–70 °C. Without the added esters, no living polymerizations occurred. The number-average molecular weights of the living polymers increased in direct proportion to monomer conversion, were inversely proportional to the concentration of initiator 1, but were independent of that of $EtAlCl_2$; the polymers invariably had very narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n \leq 1.1$). The rate of the polymerization by 1/$EtAlCl_2$ in the presence of the added ester was much lower than in its absence and depended on its carbonyl substituent R ($C_6H_5 > CH_3 \sim OC_2H_5$). It was proposed that the propagating species is stabilized by the added ester through its nucleophilic interaction with the cationic site.

Introduction

In our recent publications, we have reported the living cationic polymerization of isobutyl vinyl ether (IBVE) initiated with ethylaluminum dichloride ($EtAlCl_2$) in the presence of inert bases such as esters (e.g., ethyl acetate)[2] or ethers (e.g., dioxane).[3] The unique features of these processes include (1) the use of $EtAlCl_2$, a metal halide that is commonly applied to nonliving cationic polymerization; (2) the formation of living polymers even at +25 °C, much higher than the cryogenic temperatures (below −100 °C) often required for the production of high polymers with $EtAlCl_2$; and most important, (3) the necessity of a large excess of added bases over $EtAlCl_2$ (e.g., 25- to 250-fold molar excess for ethyl acetate).

Another class of the initiating systems that afford living cationic polymerization involves combinations of hydrogen iodide and iodine[4] or zinc halides[5,6] (HI/I_2 and HI/ZnX_2, respectively). The living processes using $EtAlCl_2$ are based on a concept "stabilization of the growing carbocation by *added bases*" which fundamentally differs from that for the HI/I_2 and HI/ZnX_2 systems ("stabilization of the growing carbocation by *counteranions*");[7] for the latter, the strong nucleophilic interaction of the iodide counteranion with the propagating carbocation is crucial for the generation of the living species. Kennedy's initiating systems, consisting of boron trichloride and tertiary esters[8] or ethers,[9] appear to follow the second approach, although they formally resemble our aluminum-based system with excess esters or ethers (see below).

The concept "stabilization of the growing carbocation by added bases" implies that living polymerization may proceed where an externally added ester or ether stabilizes an otherwise unstable growing carbocation which is accompanied by a weakly nucleophilic, noninteracting counterion;[7] the anion generated by $EtAlCl_2$ is most likely of this type. Despite some phenomenological evidence,[2,3] however, the details of the $EtAlCl_2$-mediated living polymerization in the presence of externally added bases and, in turn, the generality of our concepts for carbocation stabilization remain unknown.

The objects of this study, therefore, were to clarify (1) which basic compounds are suited for stabilizing growing carbocations and (2) the nature of the propagating species that are thus stabilized and exhibit the living character. We employed herein three esters ($RCOOC_2H_5$; R = CH_3, C_6H_5, OC_2H_5) and related carbonyl compounds (acetic anhydride and *N*,*N*-dimethylacetamide) and examined possible living polymerization of IBVE in their presence. Although $EtAlCl_2$ alone polymerizes IBVE and indeed gives living polymers in the presence of ethyl acetate,[2] we utilized in this work a new initiating system, consisting of $EtAlCl_2$ and the acetate of IBVE (1), that permits better control of polymer molecular weight than the organoaluminum alone does.[10] As will be shown in this paper, the 1/$EtAlCl_2$ system cleanly initiates polymerization of IBVE via complex 2, in which 1 serves as a cationogen:

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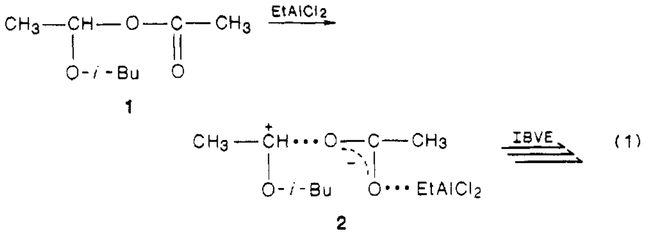


$$\underset{\textstyle\mathbf{1}}{CH_3-\underset{O\text{-}i\text{-}Bu}{CH}-O-\underset{O}{\overset{\|}{C}}-CH_3} \xrightarrow{EtAlCl_2} \underset{\textstyle\mathbf{2}}{CH_3-\underset{O\text{-}i\text{-}Bu}{\overset{+}{C}H}\cdots O\!=\!\underset{O\cdots EtAlCl_2}{C}-CH_3} \xrightarrow{IBVE} \quad (1)$$

Experimental Section

Materials. Commercial IBVE was washed with an aqueous alkali solution and then water, dried (KOH pellets), and distilled twice over calcium hydride before use. $EtAlCl_2$ was obtained commercially as an *n*-hexane solution (1.0 M; Kanto Chemicals) and used without further purification. Ethyl acetate, ethyl benzoate, ethyl carbonate, and *N,N*-dimethylacetamide (all guaranteed reagents, Wako Chemicals) were distilled twice over calcium hydride. Acetic anhydride was purified by azeotropic distillation with toluene; trace acetic acid was removed as the toluene azeotrope.[11] A solution of water was prepared by saturating purified toluene with ion-exchanged water. Trifluoroacetic acid (CF_3CO_2H) (Wako Chemicals) was used as received. *n*-Hexane as a solvent was purified by the usual methods[4a] and distilled over calcium hydride at least twice just before use.

Synthesis of the IBVE–Acetic Acid Adduct (1).[12] This was prepared by treatment of IBVE (87.4 mL, 0.75 mol) with acetic acid (28.6 mL, 0.50 mol) at 60 °C in 3 h. The crude product was distilled twice over calcium hydride under reduce pressure (61 °C (20 Torr)) to give 1 as a sweet smelling colorless oil: 85% isolated yield from acetic acid; purity >99%. ^1H NMR δ 5.9 (q, 1 H, OCHO), 3.3 (m, 2 H, OCH_2C), 2.1 (s, 3 H, $OCOCH_3$), 1.8 (m, 1 H, $CCHMe_2$), 1.4 (d, 3 H, CH_3C), 0.9 (d, 6 H, $C(CH_3)_2$); ^{13}C NMR δ 170.3 (C=O), 96.2 (OCHO), 75.7 (OCH_2), 28.2 (CH), 19.0, 20.4, 20.9 (all CH_3).

Polymerization 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 1 (or water or CF_3CO_2H) and $EtAlCl_2$ into a monomer solution containing an ester additive and quenched with ammoniacal methanol. The quenched reaction mixtures were sequentially washed with dilute hydrochloric acid and with water to remove the initiator residues, evaporated to dryness under reduced pressure, and vacuum dried overnight to give the product polymers. The conversion of IBVE was measured by gravimetry of the product.

Polymer Characterization. The MWD of poly(IBVE) was determined by size-exclusion chromatography (SEC) in chloroform on a JASCO Trirotar chromatograph equipped with polystyrene gel columns (Shodex A-802 and A-804 (×2); 8.0 mm i.d. × 500 mm each). The number-average molecular weight ($\bar{M}_n$) and polydispersity ratio ($\bar{M}_w/\bar{M}_n$) were calculated from SEC curves on the basis of a polystyrene calibration. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX90Q spectrometer in $CDCl_3$.

Results and Discussion

1. Polymerization in the Presence of Ethyl Acetate.

Following our preliminary study using $EtAlCl_2$ alone,[2] we first investigated the effects of externally added ethyl acetate on the IBVE polymerization by the $1/EtAlCl_2$ and related initiating systems.

Polymerization by $1/EtAlCl_2$ at 0 °C. IBVE was polymerized by a mixture of adduct 1 and $EtAlCl_2$ (1:5 molar ratio) in *n*-hexane at 0 °C either in the presence or absence of excess ethyl acetate. As Figure 1 shows, the polymerization in the absence of ethyl acetate was so rapid as to be completed in 5 min, but addition of the ester (1.0 M; 50-fold molar excess over $EtAlCl_2$) remarkably retarded the reaction. The retarded polymerization by $1/EtAlCl_2$, however, was much faster than that with $EtAlCl_2$ alone in the presence of the same amount of ethyl acetate. In contrast, adduct 1 alone was totally unable to polymerize IBVE otherwise under the same conditions (the square in Figure 1). Thus, 1 works as a cationogen that needs $EtAlCl_2$ for initiating IBVE polymerization (eq 1); further evidence for this mechanism will be presented later in this paper.

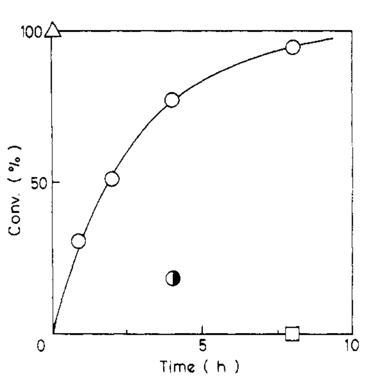


Figure 1. Effect of ethyl acetate on the polymerization of IBVE by $1/EtAlCl_2$ in *n*-hexane at 0 °C and $[IBVE]_0 = 0.76$ M (10 vol %): (○) $[1]_0 = 4.0$ mM, $[EtAlCl_2]_0 = 20$ mM, $[CH_3COOEt] = 1.0$ M; (△) without CH_3COOEt, (□) without $EtAlCl_2$, (◑) without 1 but otherwise under the same conditions as for the data designated by open circles.

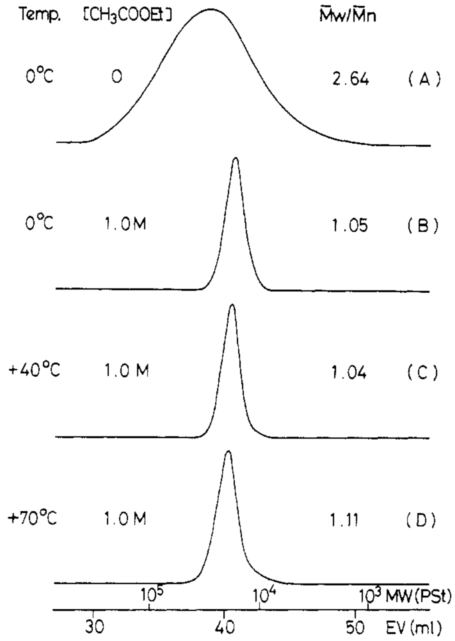


Figure 2. MWD of poly(IBVE) obtained by $1/EtAlCl_2$ in *n*-hexane at 0–70 °C in the presence (B–D) and absence (A) of ethyl acetate: $[IBVE]_0 = 0.76$ M (10 vol %); $[1]_0 = 4.0$ mM; $[EtAlCl_2]_0 = 20$ mM (0 °C) or 4.0 mM (+40 and +70 °C); $[CH_3COOEt] = 1.0$ M; conversion ≥94%.

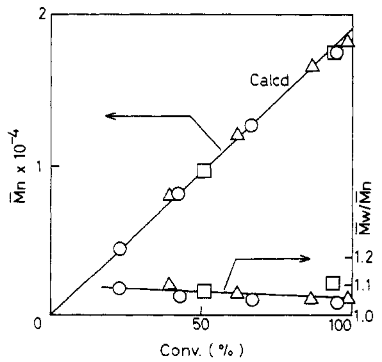


Figure 3. Conversion dependence of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of poly(IBVE) obtained by $1/EtAlCl_2$ in *n*-hexane at 0–70 °C in the presence of ethyl acetate: $[IBVE]_0 = 0.76$ M (10 vol %); $[1]_0 = 4.0$ mM; $[EtAlCl_2]_0 = 10$ mM (0 °C) or 4.0 mM (+40 and +70 °C); $[CH_3COOEt] = 1.0$ M. Polymerization temperature (°C): (△) 0; (○) +40; (□) +70. The diagonal solid line indicates the calculated $\bar{M}_n$ for living polymers (=(wt of polymerized IBVE per L)/$[1]_0$).

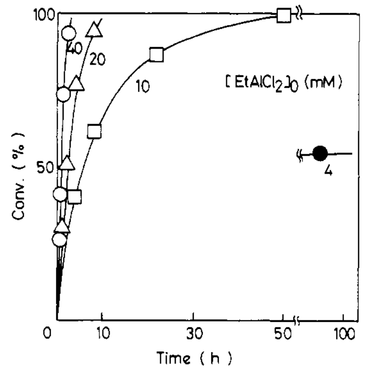


Figure 4. Effect of $EtAlCl_2$ concentration on the polymerization of IBVE by $1/EtAlCl_2$ in *n*-hexane at 0 °C in the presence of ethyl acetate: $[IBVE]_0$ = 0.76 M (10 vol %); $[1]_0$ = 4.0 mM; $[CH_3COOEt]$ = 1.0 M. $[EtAlCl_2]_0$ (mM): (●) 4.0; (□) 10; (△) 20; (○) 40.

Figure 2A,B illustrates the MWD of the polymers produced by $1/EtAlCl_2$ in the presence and absence of ethyl acetate (conversion >94%). The presence of the ester resulted in polymers with a nearly monodisperse MWD ($\bar{M}_w/\bar{M}_n$ = 1.05), whereas those obtained in its absence exhibited a much broader distribution ($\bar{M}_w/\bar{M}_n$ = 2.6).

Figure 3 (triangles) plots the $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of the polymers obtained in the presence of ethyl acetate, as a function of IBVE conversion. The polymer molecular weight was directly proportional to conversion, and the $\bar{M}_w/\bar{M}_n$ ratios stayed below 1.1, even decreasing slightly from this value at higher conversions. The $\bar{M}_n$ values, though based on a polystyrene calibration, were in excellent agreement with the calculated values, assuming that one polymer chain forms per unit cationogen 1. All these facts demonstrate the living nature of the polymerization by $1/EtAlCl_2$ at 0 °C in the presence of excess ethyl acetate.

Living Polymerization above Room Temperature. Particularly interesting is that the presence of ethyl acetate led to similar living polymerizations not only at 0 °C but also at higher temperatures up to +70 °C, where conventional cationic polymerizations of vinyl ethers suffer from dominant chain transfer and other side reactions to yield oligomers only.[13]

Thus, the polymerizations of IBVE by $1/EtAlCl_2$ were carried out at +40 and +70 °C in the presence of ethyl acetate; the overall reaction rate increased with elevating temperature. The MWDs of the product polymers were quite narrow ($\bar{M}_w/\bar{M}_n \leq 1.1$), although slightly broadening at 70 °C (Figure 2C,D; see also Figure 3). The living nature of the polymerizations was established by linear increases in the polymers' $\bar{M}_n$ in direct proportion to conversion, as well as their excellent agreement with the calculated values for living polymers (one chain per unit cationogen 1) (Figure 3, circles and squares). It should also be noted that such high-temperature living processes are first achieved with use of the $1/EtAlCl_2$ initiating system; $EtAlCl_2$ alone (with adventitious water[10]) affords living polymers only below +25 °C even in the presence of ethyl acetate.[2]

Effects of the Concentrations of 1 and $EtAlCl_2$. The polymerization by $1/EtAlCl_2$ in the presence of ethyl acetate was carried out at 0 °C at constant initial concentrations of IBVE and 1, while that of $EtAlCl_2$ was varied ($EtAlCl_2/1$ = 1–10 molar ratio). The reaction monotonously accelerated with increasing $EtAlCl_2$ concentration (Figure 4); i.e., the half-life period of the monomer decreased as follows: 90 h ($[EtAlCl_2]_0$ = 4.0 mM) > 6 h (10 mM) > 2 h (20 mM) > 0.5 h (40 mM). Despite such rate differences, all these polymerizations proved living. As Figure 5 shows, the $\bar{M}_n$'s of the polymers increase in direct proportion to monomer conversion, and more important, they are independent of the concentration of $EtAlCl_2$, giving a single straight line passing through the origin; the MWDs of the polymers were invariably very narrow.

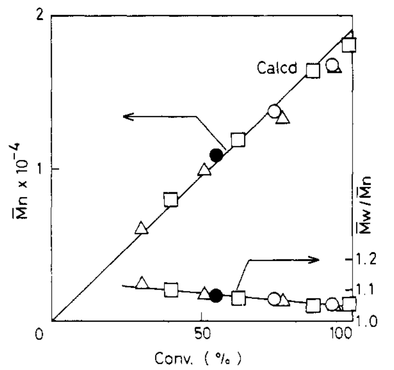


Figure 5. Conversion dependence of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of poly(IBVE) obtained by $1/EtAlCl_2$ in *n*-hexane at 0 °C in the presence of ethyl acetate at varying $[EtAlCl_2]_0$: $[IBVE]_0$ = 0.76 M (10 vol %); $[1]_0$ = 4.0 mM; $[CH_3COOEt]$ = 1.0 M. $[EtAlCl_2]_0$ (mM): (●) 4.0; (□) 10; (△) 20; (○) 40. The diagonal solid line indicates the calculated $\bar{M}_n$ for living polymers (=(wt of polymerized IBVE per L)/$[1]_0$).

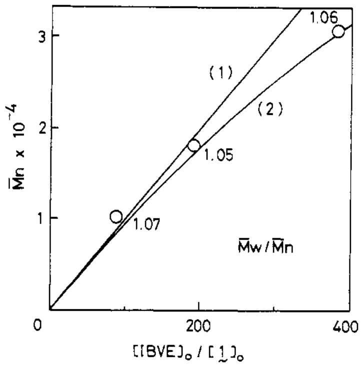


Figure 6. $\bar{M}_n$ values of poly(IBVE) obtained by $1/EtAlCl_2$ in *n*-hexane at 0 °C in the presence of ethyl acetate as a function of $[IBVE]_0$/[living end]: $[IBVE]_0$ = 0.76 M (10 vol %); $[EtAlCl_2]_0$ = 10 mM; $[1]_0$ = 2.0, 4.0, and 8.0 mM. Calcd $\bar{M}_n(1)$ = (wt of polymerized IBVE per L)/$[1]_0$ and calcd $\bar{M}_n(2)$ = (wt of polymerized IBVE per L)/($[1]_0$ + $[H_2O]$), where $[H_2O]$ is the concentration of adventitious water in the reaction mixtures (assumed to be 0.5 mM).

Another series of the polymerization was performed with constant initial amounts of IBVE and $EtAlCl_2$ but at variable concentrations of 1 (Figure 6). The polymer molecular weights were inversely proportional to the latter variable, maintaining the $\bar{M}_w/\bar{M}_n$ ratios below 1.1. Closer inspection of the plot revealed, however, that the $\bar{M}_n$ value for the lowest concentration of 1 (IBVE/1 = 380) is about 20% lower than the calculated value (line 1 in Figure 6). Since, for this particular run, the concentrations of 1 (2.0 mM) and adventitious water (ca. 0.5 mM) are comparable, the lower $\bar{M}_n$ may be due to the parallel initiation by the two. In fact, if we assume that [living end] = $[1]_0$ + $[H_2O]$, the observed molecular weight is very close to the calculated value (curve 2 in Figure 6).

The data collected in Figures 5 and 6 show, therefore, the molecular weight of the living polymers to be dependent on the concentration of 1 but independent of that of $EtAlCl_2$. This finding, coupled with the absence of polymerization by 1 alone (Figure 1), shows that 1 is responsible for generation of the initiating/propagating species, whereas $EtAlCl_2$ accelerates their propagation. Accordingly, 1 is an *initiator* (cationogen), while $EtAlCl_2$

Table I
Living Polymerization of IBVE by Protogen (or 1)/$EtAlCl_2$ Systems in the Presence of Ethyl Acetate in *n*-Hexane at 0 °C[a]

initiator	time, h	conv, %	$\bar{M}_n$(obsd)	$\bar{M}_n$(calcd)[b]	$\bar{M}_w/\bar{M}_n$
1	8.0	94	16600	17900	1.05
H_2O	6.5	92	16400	17500	1.09
CF_3CO_2H	4.0	89	15700	16900	1.07

[a] $[M]_0$ = 0.76 M; $[\text{initiator}]_0$ = 4.0 mM; $[EtAlCl_2]_0$ = 20 mM; [ethyl acetate] = 1.0 M. [b] $\bar{M}_n$(calcd) = (% conv)(molec wt of IBVE)$[M]_0$/100$[\text{initiator}]_0$.

acts as an *activator* (or catalyst), and both cooperatively initiate IBVE polymerization, most likely via their complex 2 (eq 1). A similar complexation and activation of carboxylate or phosphate functions by organoaluminum compounds has been proposed by Nozaki and co-workers.[14]

Polymerization by Protogen/$EtAlCl_2$ Systems. Since cationogen 1 is the adduct of acetic acid with IBVE, it then follows that when coupled with $EtAlCl_2$, similar protonic acids and related protogens may polymerize IBVE and may even lead to living polymerization in the presence of ethyl acetate. We thus employed water and CF_3CO_2H as protogens (initiators) and polymerized IBVE by the protogen/$EtAlCl_2$ initiating systems at 0 °C in *n*-hexane containing excess ethyl acetate. Table I summarizes the results along with the corresponding data for the 1/$EtAlCl_2$ system.

With both protogens, the polymerizations proceeded without an induction phase to reach quantitative conversion in 5–10 h. The product polymers exhibited very narrow MWDs ($\bar{M}_w/\bar{M}_n \leq 1.1$), and their $\bar{M}_n$'s were in good agreement with the calculated values, assuming the forming of one polymer chain per unit protogen. Polymerizations in the absence of ethyl acetate but otherwise under the same conditions were much faster and led to polymers with broader MWDs. These results show the combinations of protogens and $EtAlCl_2$ to induce living IBVE polymerization as the 1/$EtAlCl_2$ system does; the critical role of added ethyl acetate in attaining these living processes is again obvious.

Separate control experiments revealed that water and CF_3CO_2H alone are totally unable to polymerize IBVE under our conditions. It is important, however, that CF_3CO_2H instead gave in quantitative yield an adduct with IBVE [$CH_3CH(O\textit{i}Bu)OCOCF_3$] that is structurally similar to the acetate version 1: ^1H NMR ($CDCl_3$) δ 6.1 (q, 1 H, OCHO), 3.4 (m, 2 H, OCH_2C), 1.9 (m, 1 H, $CC\textit{H}Me_2$), 1.6 (d, 3 H, CH_3C), 0.9 (d, 6 H, $C(CH_3)_2$). This finding indicates the similarity in mechanism between the living polymerizations initiated by the protogen/$EtAlCl_2$ systems and by the 1/$EtAlCl_2$ counterpart.

Closer inspection of Table I further reveals a dependence of the polymerization rate on the protogens in the order: 1 (or CH_3CO_2H) < H_2O < CF_3CO_2H. Accordingly, even in the presence of excess ethyl acetate that no doubt interacts strongly with the growing carbocation, the counteranions derived from these protogens and $EtAlCl_2$ still maintain some interaction with their cationic partners.

2. Polymerization in the Presence of Other Esters and Related Compounds. In addition to counteranions (initiators), another factor that may affect the living polymerizations by the 1 (or protogen)/$EtAlCl_2$ initiating system is of course the structure and basicity of externally added bases. As such basic compounds other than ethyl acetate, we herein selected ethyl benzoate and carbonate, as well as related carbonyl compounds (acetic anhydride and *N*,*N*-dimethylacetamide), and in their presence the polymerization of IBVE by 1/$EtAlCl_2$ was carried out in *n*-hexane solvent at +40 °C. The concentrations of the added bases were all 1.0 M, 250-fold molar excess over 1 and $EtAlCl_2$.

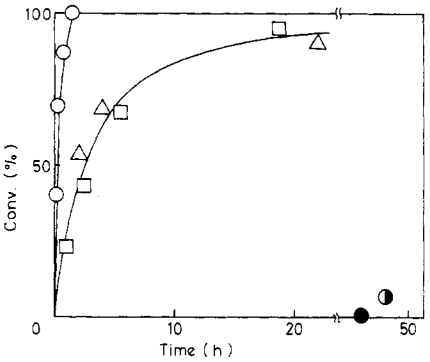


Figure 7. Time–conversion curves for the polymerization of IBVE by 1/$EtAlCl_2$ in *n*-hexane at +40 °C in the presence of added bases: $[IBVE]_0$ = 0.76 M (10 vol %); $[1]_0$ = $[EtAlCl_2]_0$ = 4.0 mM. Added bases (1.0 M): (□) ethyl acetate; (○) ethyl benzoate; (△) ethyl carbonate; (◐) acetic anhydride; (●) *N*,*N*-dimethylacetamide.

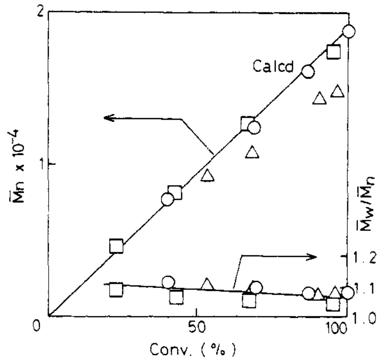


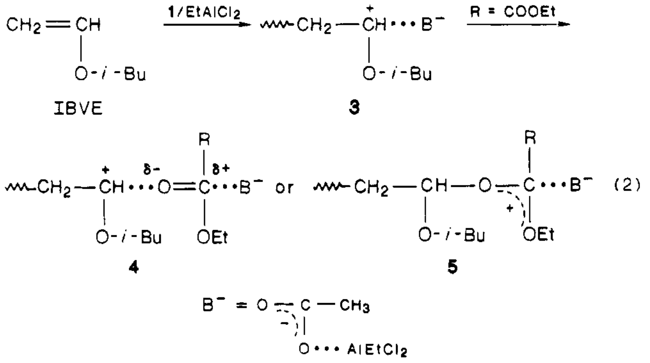
Figure 8. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of poly(IBVE) obtained by 1/$EtAlCl_2$ in *n*-hexane at +40 °C in the presence of added esters: $[IBVE]_0$ = 0.76 M (10 vol %); $[1]_0$ = $[EtAlCl_2]_0$ = 4.0 mM. Added esters (1.0 M): (□) ethyl acetate; (○) ethyl benzoate; (△) ethyl carbonate.

Ethyl Benzoate and Carbonate. Along with ethyl acetate, these esters fit a general formula $R\text{-}COOC_2H_5$ where R = CH_3, C_6H_5, and OC_2H_5. As Figure 7 shows, the polymerization in the presence of excess ethyl benzoate was about an order of magnitude faster than that with ethyl acetate, though being much slower than in the absence of the benzoate. The use of ethyl carbonate, on the other hand, led to a polymerization rate comparable to that with ethyl acetate. Thus, the reaction rate depends clearly on the carbonyl substituents R of the esters (R = C_6H_5 > CH_3 ~ OC_2H_5), and such a dependence in turn provides further evidence for a crucial role of the added esters in determining the (living) nature of the propagating species. The faster polymerization with ethyl benzoate is apparently attributed to the fact that, because of the conjugation between the phenyl and carbonyl groups, the aromatic ester is less basic than ethyl acetate (pK_a = −6.5 versus −7.4)[15] and hence interacts less strongly with the growing carbocation (see below).

Though differing in rate, the polymerizations in the presence of the three esters all proved living (Figure 8) and yielded narrowly distributed polymers ($\bar{M}_w/\bar{M}_n \leq 1.1$). Their $\bar{M}_n$'s were directly proportional to monomer conversion, and more important, they were virtually independent of the kind of added esters and in good agreement with the calculated values for living polymers (one chain per unit cationogen 1). The slightly lower $\bar{M}_n$ values for ethyl carbonate are due most likely to its higher moisture content, which is difficult to reduce by conventional distillation. Evidently, the added esters do not alter the initiation process but simply render the propagating species less reactive and living.

Related Carbonyl Compounds. In sharp contrast to the carboxylate esters, acetic anhydride and *N*,*N*-dimethylacetamide strongly retarded or almost inhibited the polymerization by $1/EtAlCl_2$ when added to the reaction mixtures (Figure 7). These polar carbonyl compounds may have formed stable complexes with $EtAlCl_2$, similar to the acetic anhydride–$AlCl_3$ complex,[16] that in effect sequester the organoaluminum from activating 1.

3. Nature of the Living Propagating Species. The present work has established that the presence of excess carboxylate esters $R\text{-}COOC_2H_5$ permits well-defined living polymerization of IBVE by the $1/EtAlCl_2$ and related protogen/$EtAlCl_2$ initiating systems, which otherwise induce rapid, nonliving polymerizations. The latter fact shows that the growing species (**3** in eq 2) derived from the $EtAlCl_2$-based initiating systems are per se unstable, and this instability is most likely attributed to the poorly nucleophilic, noninteracting counteranion B^- where the anionic charge is highly delocalized via complexation with $EtAlCl_2$.



The unstable species **3** is then stabilized by an added ester via its interaction with the carbocationic site, forming a living growing end (**4** and/or **5**) free from chain transfer, termination, and other undesirable side reactions. The interaction of the esters is strong and most probably involves their nucleophilic carbonyl groups, as indicated by the marked deceleration of the polymerization in the presence of esters (Figure 1), as well as by the dependence of the reaction rate on their carbonyl substituents R (Figure 7). At present, however, we cannot decide whether the interaction (stabilization) is via a simple nucleophilic solvation (**4**) or via formation of a stable dioxycarbenium ion (**5**). In any case, it is interesting that the acetate "anion" complexed with $EtAlCl_2$ appears less nucleophilic than "neutral" carboxylate esters. The ester, added in large excess over $EtAlCl_2$, may form a complex not only with the growing carbocation **2** but with free $EtAlCl_2$ as well; this complexation reduces the Lewis acidity of the organoaluminum and thereby may suppress side reactions mediated by it.

The new initiating system, $CH_3CH(OiBu)OCOCH_3$ (**1**)/$EtAlCl_2$, is formally very similar to Kennedy's $R'OCOCH_3/BCl_3$ systems (R′ = *tert*-butyl, cumyl, etc.) that permit living polymerization of isobutene;[8] both involve a metal halide complexed acetate anion as counteranion. As shown in this study, however, the two systems are fundamentally different; namely, for attaining living processes, the $1/EtAlCl_2$ system needs an excess of an added ester, whereas the $R'OCOCH_3/BCl_3$ counterpart does not. For the latter, the BCl_3-complexed acetate anion itself appears to be nucleophilic enough for the stabilization of the isobutene cation. In contrast, the $EtAlCl_2$-complexed acetate anion is not nucleophilic enough for the more stable vinyl ether cation and thus requires cation stabilization by an externally added base.

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Registry No. 1, 114043-46-8; poly(IBVE), 9003-44-5; $EtAlCl_2$, 563-43-9; CH_3CO_2Et, 141-78-6; $C_6H_5CO_2Et$, 93-89-0; HCO_2Et, 105-58-8.

References and Notes

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(10) Under our reaction conditions in a dry nitrogen atmosphere, adventitious water (ca. 0.5 mM), as protogen, most likely generates the initiating carbocation with assistance of $EtAlCl_2$.[3] Thus, the concentration of the living propagating species, or the number-average molecular weight of the product polymers, is determined by the concentration of such water and thereby is rather difficult to control precisely, unless water is purposefully added to the reaction mixture; see Table I of this paper.
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