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Living Cationic Polymerization of Vinyl Monomers by Organoaluminum Halides. 4. Polymerization of Isobutyl Vinyl Ether by $EtAlCl_2$ in the Presence of Ether Additives

Yasuhisa Kishimoto, Sadahito Aoshima,[1] and Toshinobu Higashimura*

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan.
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ABSTRACT: In the presence of added ethers (1,4-dioxane, tetrahydrofuran, and diethyl ether), living cationic polymerization of isobutyl vinyl ether was achieved in *n*-hexane at 0 to +40 °C with the use of the 1-(isobutoxy)ethyl acetate ($CH_3CH(O\text{-}i\text{-}Bu)OOCCH_3$, 1)/ethylaluminum dichloride ($EtAlCl_2$) initiating system. In particular, 1,4-dioxane as an ether additive permitted a living process operable even at +70 °C. The optimum amount of the added ethers needed for the living polymerization depended on their basicity, increasing in the order THF (1–2 vol %) > 1,4-dioxane (5–10 vol %) > Et_2O (70 vol %); diisopropyl ether, less basic and more sterically hindered than diethyl ether, was unable to induce a similar living process even when employed as solvent at 0 °C. Under these living conditions the polymers exhibited very narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n \le 1.1$), and the number-average molecular weights ($\bar{M}_n$) increased in direct proportion to monomer conversion as well as to the reciprocal of the initial concentration of 1 (as cationogen). In the polymerization with added 1,4-dioxane below +40 °C, the $\bar{M}_n$ also increased on addition of a second monomer feed to a polymerized reaction mixture. For comparison, polymerizations by $H_2O/EtAlCl_2$ and $CH_3CO_2H/EtAlCl_2$ initiating systems were also carried out in the presence of the ethers.

Introduction

We have recently established a method for truly living cationic polymerizations of vinyl monomers, for the first time, based on the concept of stabilization of unstable propagating carbocations by suitably nucleophilic counteranions.[2] Another concept for living cationic polymerization, which has also proved successful more recently, invokes added inert bases for stabilization of growing carbocations associated by less nucleophilic counteranions that are per se unable to stabilize their cationic partners.[3] For example, in the presence of a large excess of an ester[4] or ether,[5] the polymerization of isobutyl vinyl ether (IBVE) with ethylaluminum dichloride ($EtAlCl_2$), in conjunction with a protogen or cationogen, yields well-defined living polymers, whereas the absence of the added base results in a transfer-dominant nonliving polymerization with other reaction conditions the same.

For esters and related carbonyl compounds, our latest study[6] has further clarified in detail which types of such oxygen bases fit for stabilizing growing cations, as well as the optimum reaction conditions for the $EtAlCl_2$-mediated living processes of IBVE in the presence of esters. It has been proposed that the basic carbonyl oxygen of an ester plays a critical role in stabilizing the otherwise unstable propagating carbocation so as to endow it with living character.

Following our preliminary report,[5] the present study is concerned with the use of a series of ethers (1,4-dioxane, tetrahydrofuran, diethyl ether, and diisopropyl ether) as basic additives that, similarly to esters, may effect living cationic polymerization of IBVE. The initiating systems employed herein are all based on $EtAlCl_2$, coupled with 1-(isobutoxy)ethyl acetate ($CH_3CH(O\text{-}i\text{-}Bu)OCOCH_3$, 1),[3] water, or acetic acid (CH_3CO_2H), as cationogen or protogen. Particular emphasis was placed on the relationship between the basicity (or structure) of the ethers and their cation-stabilizing ability.

Experimental Section

Materials. Commercial IBVE (Tokyo Kasei Kogyo) was washed with an aqueous alkaline solution and water and distilled twice over calcium hydride just before use.[4] $EtAlCl_2$ was commercially obtained as a *n*-hexane solution (1.0 M; Kanto Chemicals) and used without further purification. 1,4-Dioxane (DO), tetrahydrofuran (THF), diethyl ether (Et_2O), and diisopropyl ether (iPr_2O) (Wako Chemicals, all guaranteed reagents) were dried over calcium chloride and then distilled over calcium hydride before use. *n*-Hexane and toluene as polymerization solvents were purified by the usual method[3] and distilled twice over calcium

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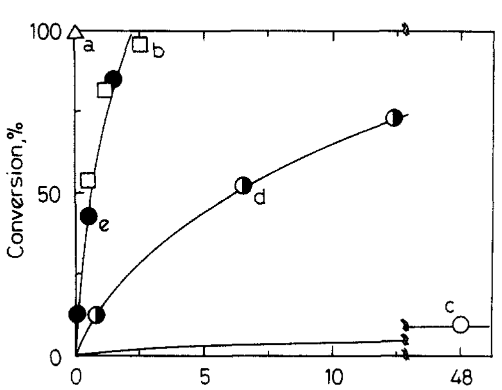


Figure 1. Time–conversion curves for the polymerization of IBVE by 1/$EtAlCl_2$ in the presence of DO in *n*-hexane at three temperatures: $[IBVE]_0 = 0.76$ M; $[1]_0 = 4.0$ mM; see the table below for symbol specification.

	symbol	DO, M	$EtAlCl_2$, mM	temp, °C
a	△	0	20	0
b	□	1.2	20	0
c	○	1.2	4.0	0
d	◑	1.2	4.0	+40
e	●	1.2	4.0	+70

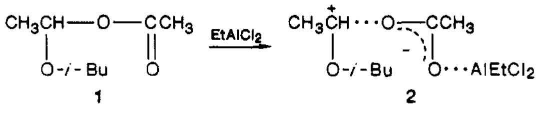
hydride just before use. A solution of water (22 mM) in toluene was prepared by saturating ion-exchanged water in the solvent. Commercial CH_3CO_2H (Wako Chemicals, guaranteed reagent) was dried over calcium chloride and distilled twice over phosphorus pentoxide before use. Cationogen 1 was prepared from IBVE and CH_3CO_2H and distilled twice over calcium hydride under reduced pressure, as previously reported.[3]

Procedures. Polymerization was carried out at 0 to +70 °C under dry nitrogen in a baked glass tube equipped with a three-way stopcock. The reaction was initiated by addition of an $EtAlCl_2$ solution in *n*-hexane into a mixture of IBVE, an ether additive, and a cationogen or protogen in *n*-hexane at the polymerization temperature; in some cases $EtAlCl_2$ was added at −78 °C, and then the mixture was brought to the polymerization temperature. After a predetermined interval, the polymerization was quenched with ammoniacal methanol. The quenched reaction mixture was sequentially washed with 1 N hydrochloric acid and water to remove the initiator residues, neutralized with a dilute aqueous sodium hydroxide solution, evaporated under reduced pressure, and vacuum dried overnight to give the product polymer. The conversion of IBVE was measured by gravimetry of the product.

The molecular weight distribution (MWD) of the polymers was measured by size-exclusion chromatography in chloroform at room temperature on a Jasco Trirotar-II instrument equipped with three polystyrene gel columns (Shodex A-802 and A-804 (×2), 8.0 i.d. × 500 mm). The number-average molecular weight ($\bar{M}_n$) and polydispersity ratio ($\bar{M}_w/\bar{M}_n$) were calculated from size-exclusion chromatograms on the basis of a polystyrene calibration. ^1H NMR spectra were recorded on a JEOL FX-90Q spectrometer.

Results and Discussion

1. Polymerization in the Presence of 1,4-Dioxane. As shown in our previous paper,[5] the presence of excess DO (5–10 vol %) in a reaction mixture permits living polymerization of IBVE with $EtAlCl_2$ alone, where the initiator (or protogen) is the adventitious water and hence the concentration of the initiating species or polymer molecular weight is rather difficult to control. To overcome this difficulty, we employed herein the IBVE–CH_3CO_2H adduct 1 as an initiator (cationogen) in conjunction with $EtAlCl_2$ and examined the possibility of living IBVE polymerization in the presence of DO. The adduct 1 has already been shown to quantitatively form an initiating complex with $EtAlCl_2$ (2; eq 1); in the presence of an added ester, 2 readily polymerizes IBVE into living polymers, the $\bar{M}_n$ of which is regulated by the concentration of 1.[6]



$$CH_3CH(O\text{-}i\text{-}Bu)\text{—}O\text{—}C(=O)CH_3 \xrightarrow{EtAlCl_2} CH_3\overset{+}{C}H(O\text{-}i\text{-}Bu)\cdots O{=}C(CH_3)\text{—}O\cdots AlEtCl_2 \quad (1)$$

1 2

Cationogen 1/$EtAlCl_2$ Initiating System. As $EtAlCl_2$ alone does (with adventitious water as protogen),[5] the 1/$EtAlCl_2$ system rapidly polymerized IBVE in *n*-hexane at 0 to +70 °C in the absence of DO (Figure 1a). Addition of increasing amounts of the cyclic ether led to increasingly slower but still quantitative polymerizations that were invariably of first order in monomer (see Figure 8b below). As Figure 1 shows, the reactions in the presence of 10 vol % of DO (1.2 M) were faster at higher temperatures (curves c–e) or at higher concentrations of $EtAlCl_2$ (curves b and c).

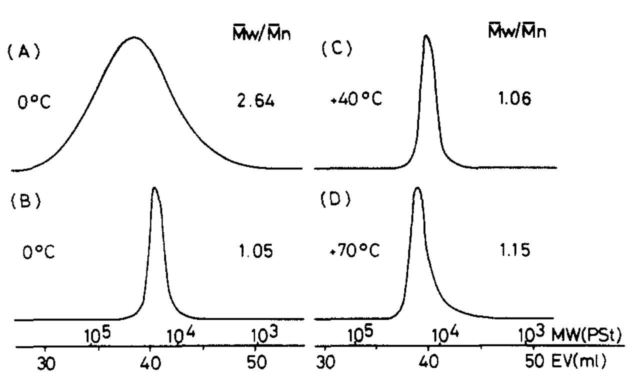


Figure 2. MWDs of poly(IBVE) obtained with 1/$EtAlCl_2$ in the presence (B–D) and absence (A) of 1.2 M DO in *n*-hexane at three temperatures: $[IBVE]_0 = 0.76$ M; $[1]_0 = 4.0$ mM; $[EtAlCl_2]_0 = 20$ mM (0 °C) or 4.0 mM (+40, +70 °C); conversion >70%.

Figure 2 shows the MWDs of the polymer obtained in the experiments for Figure 1. In contrast to the broad MWD of the polymer for the DO-free system (Figure 2A), the polymers (Figure 2B) produced at 0 °C in the presence of DO exhibit an extremely narrow MWD ($\bar{M}_w/\bar{M}_n < 1.1$). More important, similarly narrow MWDs were obtained above room temperature ($\bar{M}_w/\bar{M}_n = 1.06$ (+40 °C) and 1.15 (+70 °C); Figure 2C,D); the MWD for +70 °C was somewhat broader, however.

Figure 3 illustrates the relationship between conversion and the $\bar{M}_n$ of the polymers thus obtained in the presence of DO. At all three temperatures, the polymer's $\bar{M}_n$ was directly proportional to monomer conversion and in good agreement with the calculated value assuming that one living polymer chain forms per unit cationogen 1. Furthermore, the MWD of the polymer remained very narrow throughout the reactions ($\bar{M}_w/\bar{M}_n \leq 1.15$). These results show that living polymerization of IBVE was achieved in the presence of an excess of DO (10 vol %) with the 1/$EtAlCl_2$ initiating system at 0 °C and even above room temperature up to +70 °C.

The lifetime of the growing end, however, was shown to depend on polymerization temperature, according to so-called "monomer-addition" experiments in which a fresh feed of IBVE was added to the reaction mixture at 95–100% conversion. Figure 4 shows three pairs of the MWD curves for the polymers thus obtained before and after monomer addition. In the polymerizations at 0 and +40 °C (Figure 4A,B), the MWD remained very narrow and shifted toward high molecular weight upon the addition of IBVE. Accordingly, the $\bar{M}_n$ continued to increase proportionally to conversion and was close to the calculated value for the living polymer. Similar experiments at +70 °C resulted in much broader MWDs and no increase in $\bar{M}_n$. Therefore, perfectly living polymerization of IBVE is operable only below +40 °C; at +70 °C the growing end retains a long lifetime but is subject to chain transfer and

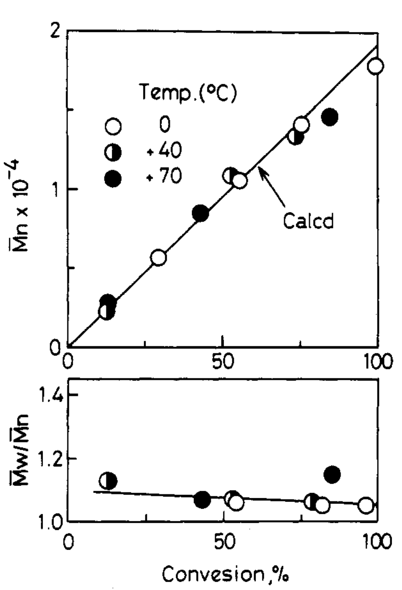


Figure 3. Relationships between conversion and the $\bar{M}_n$ or $\bar{M}_w/\bar{M}_n$ of the polymers in the polymerization of IBVE by 1/$EtAlCl_2$ at three temperatures in the presence of 1.2 M DO in *n*-hexane: $[IBVE]_0 = 0.76$ M; $[1]_0 = 4.0$ mM; $[EtAlCl_2]_0 = 10$ mM (0 °C) or 4.0 mM (+40, +70 °C). The diagonal solid line indicates the calculated $\bar{M}_n$ values assuming one polymer chain per unit 1.

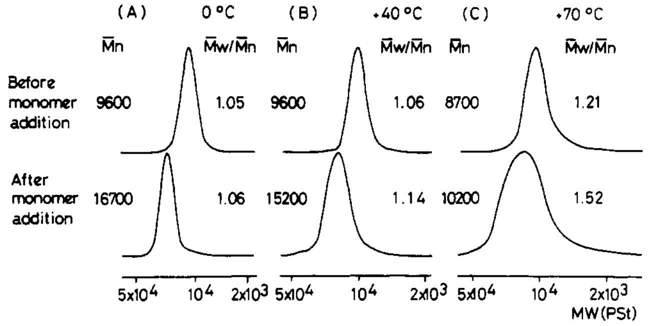


Figure 4. MWDs of poly(IBVE) obtained in monomer-addition experiments in the polymerization by 1/$EtAlCl_2$ in the presence of 1.2 M DO in *n*-hexane at three temperatures: $[IBVE]_0 = 0.38 + 0.38$ M; $[1]_0 = 4.0$ mM; $[EtAlCl_2]_0 = 20$ mM (0 °C) or 4.0 mM (+40, +70 °C). The conversions for the samples obtained before and after the monomer addition were 95–100% and 180–195%, respectively.

other chain-breaking reactions, particularly during the later stages of the polymerization.

Separate experiments revealed that the $\bar{M}_n$ of the living polymers is inversely proportional to the concentration of 1 and in good agreement with the calculated value, assuming the formation of one polymer chain per unit cationogen 1. When the concentrations of 1 and the monomer were kept constant, the polymerization rate increased with increasing $EtAlCl_2$ concentration (e.g., Figure 1b,c), whereas $\bar{M}_n$ stayed unchanged. Namely, 1 serves as an initiator, and $EtAlCl_2$ is an activator of the growing end.[3]

All these characteristics of IBVE polymerization by the 1/$EtAlCl_2$ system in the presence of DO are very similar to those for the corresponding reactions using esters in place of the cyclic ether,[6] and the use of 1 as initiator permitted precise molecular weight control of the living polymers.

Protogen/$EtAlCl_2$ Initiating Systems. For the $EtAlCl_2$-mediated living polymerizations in the presence of ester additives, we have shown not only cationogen 1 and adventitious water but also purposefully added protogens to be effective initiators.[6] In this study, we soon found that water and CH_3CO_2H, as protogens coupled with $EtAlCl_2$, similarly polymerize IBVE at 0 °C in *n*-hexane containing 10 vol % of DO (1.2 M) (Figure 5). In terms of overall rate, these polymerizations are very similar to that with the 1/$EtAlCl_2$ system (the half-filled circles), but they are much slower than the polymerization in DO-free *n*-hexane (the triangle).

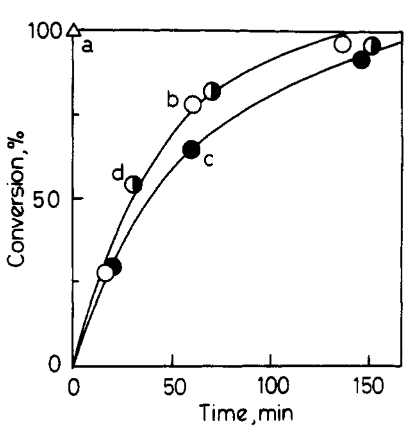


Figure 5. Time–conversion curves for the polymerization of IBVE by the protogen/$EtAlCl_2$ systems in the presence of DO in *n*-hexane at 0 °C: $[IBVE]_0 = 0.76$ M; $[EtAlCl_2]_0 = 20$ mM; see the table below for symbol specification.

	symbol	DO, M	protogen/cationogen, 4.0 mM
a	△	0	H_2O
b	○	1.2	H_2O
c	●	1.2	CH_3CO_2H
d	◑	1.2	1 (Figure 1b)

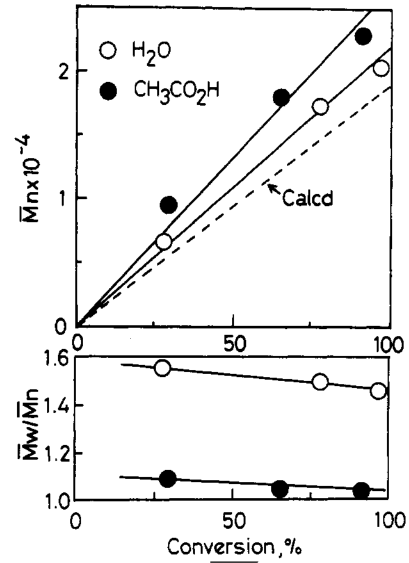


Figure 6. Relationships between conversion and the $\bar{M}_n$ or $\bar{M}_w/\bar{M}_n$ of the polymers in the polymerization of IBVE by the protogen/$EtAlCl_2$ systems in the presence of 1.2 M DO in *n*-hexane at 0 °C: $[IBVE]_0 = 0.76$ M; $[EtAlCl_2]_0 = 20$ mM. Protogen (4.0 mM): (○) H_2O; (●) CH_3CO_2H. The diagonal broken line indicates the calculated $\bar{M}_n$ values, assuming one living polymer chain per unit protogen.

As shown in Figure 6, the $\bar{M}_n$ of the polymers obtained with the $H_2O/EtAlCl_2$ initiating system increased linearly in proportion to monomer conversion and were in fair agreement with the calculated value assuming that one polymer chain forms per unit water (broken line in Figure 6). Despite such an apparently living character of the polymerization, the MWD of the polymers consisted of two peaks (Figure 7A); the one with lower molecular weight was narrow ($\bar{M}_w/\bar{M}_n \leq 1.1$) and shifted toward high molecular weight with conversion, whereas the other with high molecular weight was broad and stayed at the same position. These facts suggest the coexistence of two growing

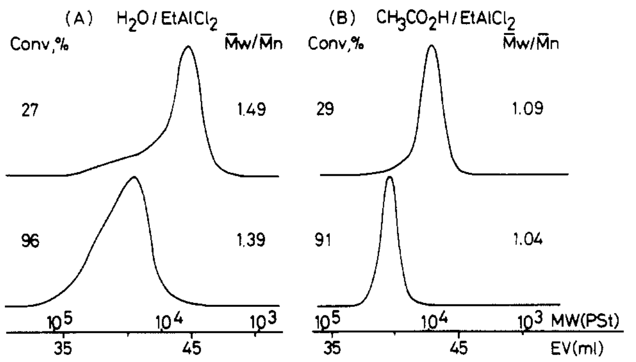


Figure 7. MWDs of poly(IBVE) obtained with (A) $H_2O/EtAlCl_2$ and (B) $CH_3CO_2H/EtAlCl_2$ in the presence of 1.2 M DO in *n*-hexane at 0 °C: $[IBVE]_0 = 0.76$ M; $[EtAlCl_2]_0 = 20$ mM; $[H_2O]_0 = [CH_3CO_2H]_0 = 4.0$ mM.

species where one is living, the other is nonliving. It remains obscure why the $H_2O/EtAlCl_2$ system specifically forms two intermediates, where the $1/EtAlCl_2$ pair generates a single living species.

The use of CH_3CO_2H as protogen led to polymers with very narrow MWDs ($\bar{M}_w/\bar{M}_n < 1.1$) (Figure 7B), the $\bar{M}_n$'s of which were directly proportional to monomer conversion but invariably higher than the calculated values (one polymer chain per unit CH_3CO_2H) (Figure 6). Thus, the $CH_3CO_2H/EtAlCl_2$ system indeed generates a living, growing species in the presence of DO but the initiation efficiency is below 100% (ca. 70% for the data shown in Figure 6).

When compared with the $1/EtAlCl_2$ system, therefore, the protogen/$EtAlCl_2$ pairs result in more complicated polymerizations, where the propagating species are of long lifetime but polymer molecular weights are difficult to control. A reason for this complexity might be the self-association of water and a free protonic acid in *n*-hexane, which would lead to the low initiation efficiency or to the formation of multiple active centers carrying different counteranions.

2. Polymerization in the Presence of Other Ethers. The achievement of the living IBVE polymerization in the presence of DO prompted us to employ other ethers as basic additives that differ in the basicity (nucleophilicity) and steric hindrance of the ether oxygen, which is most likely responsible for stabilizing the carbocationic active site. A closely related point of interest is why the monomers and polymers of vinyl *ethers* are ineffective in such cation stabilization, despite their inevitable presence in the polymerization system. With these points in mind, we employed cyclic and acyclic ethers [tetrahydrofuran (THF), diethyl ether (Et_2O), diisopropyl ether (iPr_2O), and a dead poly(IBVE) sample ($\bar{M}_n = 9800$, $\bar{M}_w/\bar{M}_n = 1.04$)] in place of DO. The basicity of these ethers, as judged from the pK_a values of their protonated forms in sulfuric acid,[7] is THF > DO > Et_2O > iPr_2O (see Table I).

In the presence of various amounts (1.6–70 vol %) of these four ethers, the polymerization of IBVE with the $1/EtAlCl_2$ system was carried out in *n*-hexane at 0 °C, for which the living character was examined as a function of the basicity and structure of the ethers.

Polymerization Rate. Figure 8 shows typical time-conversion profiles obtained with the four low molecular weight ethers at varying concentrations. In all cases, the addition of the ethers retarded the polymerization, which, however, was quantitative and free of an induction phase. The extent of the retardation was found to depend on the basicity of the added ethers; i.e., the more basic the ether is, the less is needed to attain the same reaction rate. For example, the polymerization in the presence of 1.6 vol % (0.20 M) of THF, the most basic among the four, is still slower than those with much larger amounts of DO (10 vol %; 1.2 M) and Et_2O (70 vol %; 6.7 M). In contrast, the least basic iPr_2O (70 vol %; 5.0 M) and the dead poly(IBVE) (1.2 M repeat units) were almost ineffective even when employed in large excess, leading to polymerizations as fast as that in the absence of added ethers.

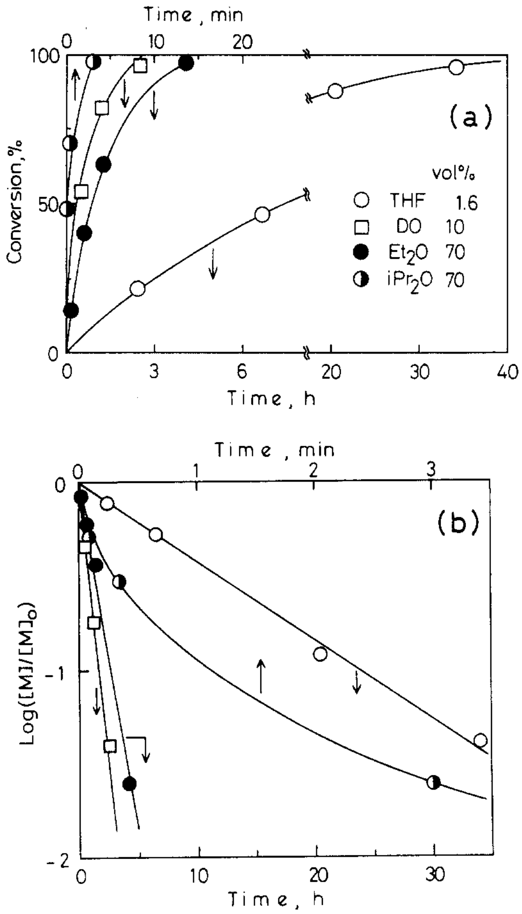


Figure 8. Time–conversion curves (a) and first-order plots (b) for the polymerization of IBVE by $1/EtAlCl_2$ in the presence of various ethers in *n*-hexane at 0 °C: $[IBVE]_0 = 0.76$ M; $[EtAlCl_2]_0 = 20$ mM; $[1]_0 = 4.0$ mM. The ethers and their amounts as indicated.

Formation of Living Polymers. As Figures 9 and 10 show, the polymers obtained in the presence of THF (1.6 vol %) and Et_2O (70 vol %) clearly had long lifetimes. They exhibited narrow MWDs, the $\bar{M}_n$'s of which increased almost proportionally to monomer conversion and rather close to the calculated values, assuming the formation of one polymer chain per unit cationogen 1 (the broken line in Figure 10). At higher conversions, however, the $\bar{M}_n$'s of the polymers obtained in the presence of Et_2O became smaller than the calculated values. In terms of the narrowness of the polymer MWD, the polymerization with THF is closer to a perfectly living process than that with Et_2O.

In contrast, no evidence for the formation of long-lived polymers was obtained for the polymerization with iPr_2O. The $\bar{M}_n$ of the products did not increase but instead slightly decreased with increasing conversion (Figure 10); they also exhibited broad MWDs ($\bar{M}_w/\bar{M}_n = 1.7$–$2.6$). Similarly, living polymerization did not occur in the presence of the poly(IBVE) sample (Figure 11), where the product consisted of two distinct fractions, one being the added polymer (without any changes in molecular weight and MWD) and the other a broadly distributed polymer

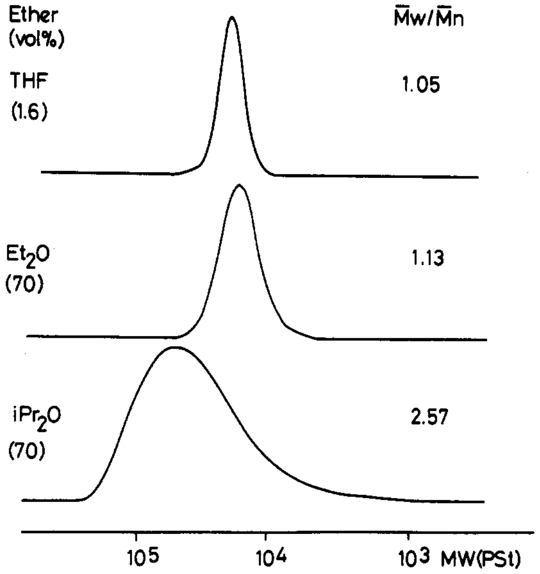


Figure 9. MWDs of poly(IBVE) obtained with $1/EtAlCl_2$ in the presence of various ethers in *n*-hexane at 0 °C: $[IBVE]_0 = 0.76$ M; $[EtAlCl_2]_0 = 20$ mM; $[1]_0 = 4.0$ mM. Conversion ca. 100%. The ethers and their amounts as indicated.

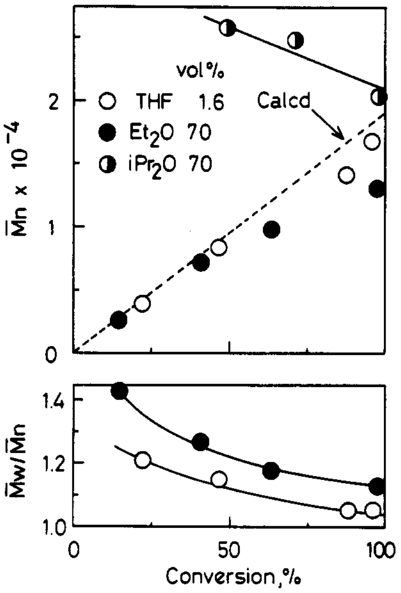


Figure 10. Relationships between conversion and the $\bar{M}_n$ or $\bar{M}_w/\bar{M}_n$ of the polymers in the polymerization of IBVE by $1/EtAlCl_2$ in the presence of various ethers in *n*-hexane at 0 °C: $[IBVE]_0 = 0.76$ M; $[EtAlCl_2]_0 = 20$ mM; $[1]_0 = 4.0$ mM. The diagonal broken line indicates the calculated $\bar{M}_n$ values, assuming one living polymer chain per unit 1. The $\bar{M}_w/\bar{M}_n$ values for iPr_2O are 1.7–2.6.

($\bar{M}_w/\bar{M}_n$ ca. 2) that was apparently produced independently of the presence of the former fraction.

Structure of the Polymers. ^1H NMR structural analysis showed the polymeric products obtained in the presence of the ethers to be invariably poly(IBVE). The spectral data failed to give evidence for the incorporation of ether-derived units into the products through ring-opening polymerization of THF etc.

3. Effect of Ether Basicity. Table I summarizes the effects of the basicity and amount of the four ethers on the living polymerization of IBVE; the living processes that were carried out under the conditions indicated with circles are already discussed above.

The data show the minimum amount of an ether for attaining a living polymerization to decrease with increasing ether basicity. For example, a small amount of 1.6 vol % suffices for the most basic THF, whereas less basic Et_2O needed a concentration as high as 70 vol %. The use of THF at higher concentrations results in unpractically slow polymerizations that apparently involve long-lived species similar to that with 1.6 vol % THF. For the less basic ethers (DO and Et_2O), the living character of the polymerization was gradually lost as their concentrations were decreased from the optimum level. A typical example is the polymerization with 10 vol % Et_2O, where the $\bar{M}_n$–conversion plot did give an uprising line but a positive intercept, indicating less precise molecular weight control.

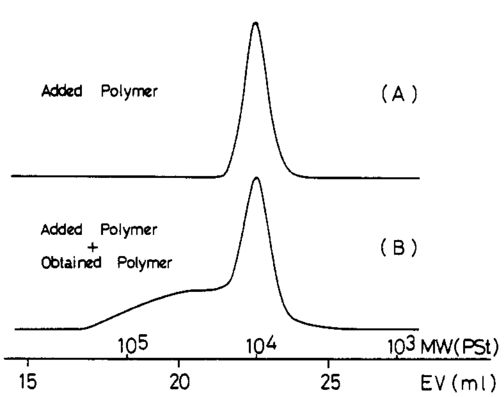


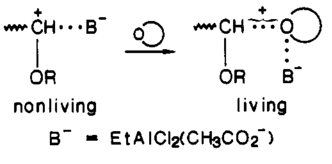
Figure 11. MWD of the product (curve B) obtained in the polymerization of IBVE with $1/EtAlCl_2$ in *n*-hexane at 0 °C in the presence of a dead poly(IBVE) sample (curve A, $\bar{M}_n = 9800$, $\bar{M}_w/\bar{M}_n = 1.04$; 1.2 M repeat units): $[IBVE]_0 = 0.76$ M; $[1]_0 = 4.0$ M; $[EtAlCl_2]_0 = 20$ mM; conversion of IBVE for sample B was 100%.

Table I
Effects of Ethers on the Living Polymerization of IBVE Initiated by the $1/EtAlCl_2$ System[a,b]

ether	pK_a[c]	concn of ether, vol %		
		1.6	10	70
THF	−2.08	○	very slow	very slow
DO	−3.22	△	○	*d*
Et_2O	−3.59	×	△	○
iPr_2O	−4.30	×	×	×

[a] Key: (○) living polymerization where $\bar{M}_n$ increases proportionally to conversion; (×) conventional polymerization where $\bar{M}_n$ is constant or decreases with conversion; (△) "imperfectly living" polymerization where the $\bar{M}_n$–conversion plot is uprising but gives a positive intercept. [b] In *n*-hexane at 0 °C; $[IBVE]_0 = 0.76$ M; $[EtAlCl_2]_0 = 20$ mM; $[1]_0 = 4.0$ mM. [c] Reference 7. [d] The polymerization solution solidified at 0 °C.

These trends summarized in Table I indicate that a more basic ether stabilizes the growing cation more strongly and/or more efficiently; and when employed at a suitable concentration, it leads to a well-defined living process. The cation stabilization by the added ether may involve a nucleophilic interaction,[5] as schematically illustrated in eq 2.



(2)

Similar oxonium ion type species are known to form in the reaction of carbenium ions with ethers and acetals.[8] It is also well-known that in cationic ring-opening polymerization of cyclic ethers and acetals, an equilibrium exist between carbenium and oxonium type intermediates.

It should be noted that iPr_2O, the least basic and most sterically crowded of the four ethers, is unable to stabilize the growing carbocation even when employed at a very high concentration. This finding accounts for the ineffectiveness of the monomer and polymer of IBVE in stabilizing the growing carbocations, although both ethereal compounds are inevitably and abundantly present in the polymerization solution. The pendant ether oxygens of poly(IBVE), on one hand, carry much bulkier substituents than that of iPr_2O does, and thereby cannot interact effectively with the cationic active site. IBVE monomer, on the other hand, would be less basic as an ether than iPr_2O, because the nonbonded electron pairs of its oxygen are conjugated with the adjacent carbon–carbon double bond. Thus there is a suitable basicity range of ethers for achieving living polymerization of vinyl ethers, which range would depend on both electric and steric factors.

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Registry No. 1, 114043-46-8; IBVE (homopolymer), 9003-44-5; EtOEt, 60-29-7; $EtAlCl_2$, 563-43-9; H_2O, 7732-18-5; CH_3CO_2H, 64-19-7; 1,4-dioxane, 123-91-1; tetrahydrofuran, 109-99-9.

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Blocked Amine Functional Initiator for Anionic Polymerization

William H. Dickstein*

IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099

C. Peter Lillya*

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003.

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ABSTRACT: Preparation and utilization of a new blocked amine functional initiator for anionic polymerization is reported. This initiator is prepared from the quantitative reaction of *sec*-butyllithium with *p*-(*N*,*N*-bis(trimethylsilyl)amino)styrene under very specific, controlled conditions. The carbanion initiator formed, unlike most blocked functional anionic initiators, is soluble in nonpolar solvents. This nonpolar solubility opens up the possibility of preparing new well-defined, end-reactive polymers, such as polysiloxanes and high *cis*-1,4-polydienes. This new initiator was used to prepare novel semitelechelic and telechelic linear poly(dimethylsiloxane)s of controlled molecular weights, narrow molecular weight distributions, and theoretical functionalities. The end-functional polymers were characterized by gel permeation chromatography, infrared spectroscopy, vapor-phase osmometry, and nuclear magnetic resonance spectroscopy.

Introduction

The field of end-reactive polymer synthesis has been active for more than 20 years. Several methods have been used to prepare end-reactive polymers including anionic,[1-10] radical,[11-14] cationic,[15-21] and group-transfer polymerizations.[22] To date, use of "living" anionic polymerization has been the most generally successful method for the preparation of end-reactive polymers with theoretical functionalities, narrow molecular weight distributions, and controlled molecular weights.[8]

End-reactive polymers can be prepared via living anionic polymerization by two primary methods.[8] To prepare telechelic polymers, one can use multifunctional anionic initiators followed by functional termination[1-5,8] or one can utilize blocked functional anionic initiators followed by multifunctional termination.[6-10] The latter method, pioneered by Schulz, has a distinct advantage over the former method. Utilization of blocked functional anionic initiators alleviates the frequently encountered problem of gelation of multiple living ends found in anionic polymerizations with multifunctional initiators.[8] This gelation problem is particularly troublesome when performing polymerizations in nonpolar solvents; however, in many cases, nonpolar solvents are the solvents of choice to achieve well-defined polymer microstructure.

Presently available blocked functional anionic initiators have, with varied levels of success, been used to prepare well-defined polymers with hydroxyl, carboxylic acid, and amine end functionalities.[6-10] However, use of the blocked functional anionic initiator method has been limited due to the insolubility in nonpolar solvents of currently reported blocked functional anionic initiators.[8] This limited initiator solubility prevents their use in the preparation of high 1,4- and *cis*-1,4-polydienes and in the preparation of well-defined telechelic poly(dimethylsiloxane)s. Only a blocked hydroxyl functional anionic initiator has shown any solubility in benzene;[10] however, this initiator is not soluble in hexanes,[6] which limits its use to prepare polydienes with the highest cis-1,4 content.

This paper will outline the preparation and use of a new blocked amine functional anionic initiator that is soluble in nonpolar solvents. The preparation of well-defined, end-reactive, amine functional poly(dimethylsiloxane)s utilizing this new initiator will be reported.

Experimental Section

Materials. *p*-Aminostyrene (PAS, 1) was obtained from Polysciences and vacuum distilled from calcium hydride. Chlorotrimethylsilane and dichlorodimethylsilane were obtained from Aldrich, distilled, and titrated prior to use. *N*,*O*-Bis(trimethylsilyl)acetamide (BSA) was obtained from Sigma and used as

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