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Living cationic polymerization of vinyl monomers by organoaluminum halides

2. $EtAlCl_2$/dioxane initiating system for living polymerization of isobutyl vinyl ether

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SUMMARY

Well-defined living polymers of isobutyl vinyl ether were obtained in the polymerization initiated with ethylaluminum dichloride ($EtAlCl_2$) in conjunction with a stoichiometric excess of dioxane (5-10 vol%) in n-hexane at 0°C. Under these conditions, the number-average molecular weight of the polymers increased in direct proportion to monomer conversion, while the molecular weight distribution stayed narrow ($\bar{M}_w/\bar{M}_n$ = 1.1-1.25). In sharp contrast, the $EtAlCl_2$-initiated polymerization in the absence of dioxane led to non-living polymers with a broad molecular weight distribution. It was concluded that the propagating carbocation is stabilized not by the counteranion but by an externally added basic compound (dioxane) that strongly interacts with the active end.

INTRODUCTION

Living polymerization is an important tool to synthesize macromolecules endowed with controlled molecular weight and structure. For achieving hitherto difficult living cationic polymerization of vinyl compounds, we pointed out the importance of counteranions that interact strongly with the propagating carbocations and thereby stabilize the active ends (1). On the basis of this working hypothesis, we in fact found living cationic polymerizations of p-methoxystyrene (2), vinyl ethers (3), and N-vinylcarbazole (4) with the use of the iodide anion as the counterion. In these living systems, the long lifetime of the growing species arises from its stabilization by the strong cation-anion interaction.

Another example in this line was recently reported by Faust and Kennedy who obtained living poly(isobutylene) by using the tertiary acetate/boron trichloride initiating systems (5). In these living processes, also, the strong interaction between the growing carbocation and the carboxylate counteranion apparently plays a critical role in forming living polymers.

A common characteristic of the iodide and carboxylate counteranions is that they are highly nucleophilic and can form a covalent bond with a growing carbocation. It is thus important whether living cationic polymerization is feasible only when the counteranion is capable of giving a covalent terminal linkage. In the first study of this series (6), we found that cationic polymerization of vinyl ethers initiated with ethylaluminum dichloride ($EtAlCl_2$) in the presence of an excess of a carboxylic acid ester leads to living polymers. Although the organoaluminum per se is expected to give a counteranion that would be unable to form a covalent bond with a carbocation, the coexistence of the added carboxylate renders

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the nature of the living propagating species obscure. The ester in conjunction with $EtAlCl_2$ may yield a carboxylate anion which forms an ester propagating species [-CH(OR)-OCOR']. Alternatively, the added ester may stabilize the growing carbocation simply by solvation.

In this second study, we utilized dioxane (DO), in place of carboxylates in the $EtAlCl_2$/ester initiating systems. Our primary object was to examine the possibility of living cationic polymerization of isobutyl vinyl ether (IBVE) with $EtAlCl_2$ in the presence of this cyclic ether that cannot form a covalent terminal group but would stabilize the propagating carbocation by solvation or other strong nucleophilic interaction.

EXPERIMENTAL

Materials

The monomer (IBVE), solvent (*n*-hexane), and initiator ($EtAlCl_2$) were purified as reported (6). DO was dried over calcium chloride and then distilled twice over calcium hydride just before use.

Procedures

Polymerization was carried out at 0°C under dry nitrogen (6). The number-average molecular weight ($\bar{M}_n$), molecular weight distribution (MWD), and polydispersity ratio ($\bar{M}_w/\bar{M}_n$) of the product polymers were measured by size-exclusion chromatography on the basis of a polystyrene calibration (6).

RESULTS

The effects of added DO were studied in the polymerization of IBVE with $EtAlCl_2$ in *n*-hexane at 0°C. As shown in Figure 1, the polymerization in the absence of DO was so rapid as to reach completion within 30 sec.

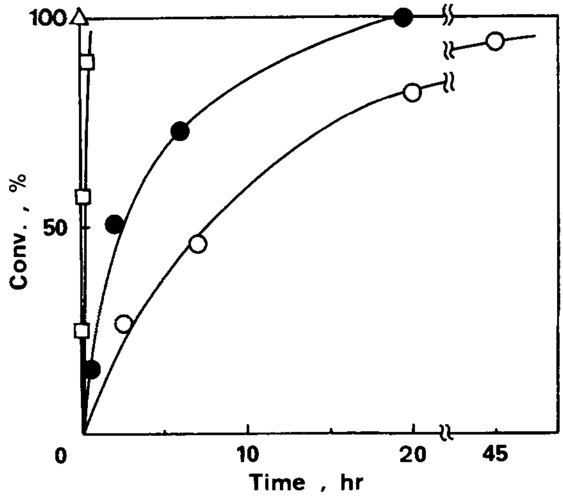


Figure 1. Time-conversion curves for the polymerization of IBVE with $EtAlCl_2$ in *n*-hexane at 0°C in the presence and absence of dioxane: $[IBVE]_0$ = 0.76 M (10 vol%); $[EtAlCl_2]_0$ = 20 mM. Dioxane in vol%: (△) none; (□) 0.43; (●) 5.0; (○) 10.

Addition of DO to the polymerization system clearly retarded the reaction where the overall rate progressively decreased with increasing amount of the added ether. These effects suggest a decrease in the reactivity of the propagating species by the interaction with nucleophilic DO.

Quite interesting is that the MWD of the product polymers remarkably depended on the amount of added DO (Figure 2). The samples obtained in the absence of the ether exhibited a broad MWD (curve A). The polymer MWD became progressively narrower as the concentration of DO was increased, and a very narrow distribution ($\bar{M}_w/\bar{M}_n$ = 1.1-1.25; curve D) was observed for the highest DO concentration (10 vol%; 1.17 M).

Addition of DO also affected the dependences of the molecular weight ($\bar{M}_n$) and MWD ($\bar{M}_w/\bar{M}_n$) of the polymers on monomer conversion (Figure 3). In the polymerization in the absence of DO, the $\bar{M}_n$ decreased with conversion, and the polydispersity ratios were invariably above 2. For DO concentration $\geq$ 5.0 vol%, in contrast, the polymer molecular weight increased

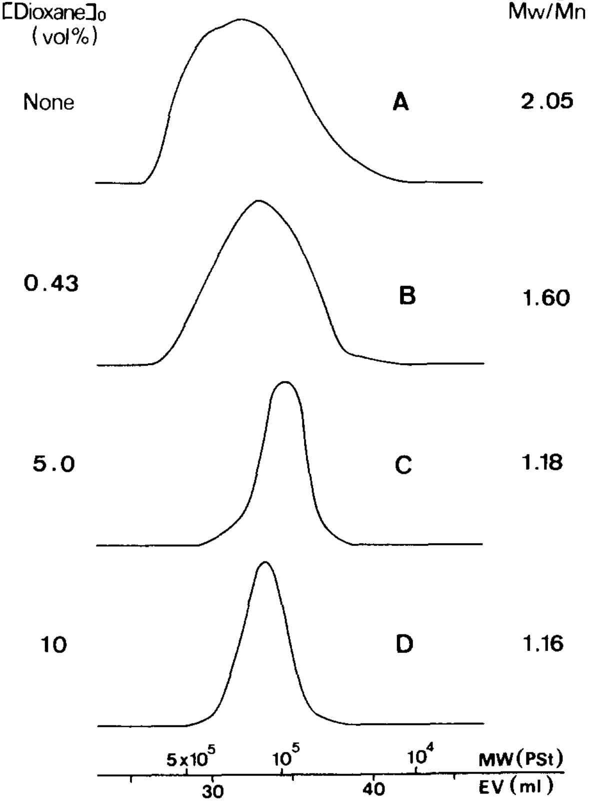


Figure 2. Effects of dioxane on the MWD of poly(IBVE) obtained with $EtAlCl_2$ in n-hexane at 0°C: $[IBVE]_0$ = 0.76 M (10 vol%); $[EtAlCl_2]_0$ = 20 mM. IBVE conversion and $\bar{M}_n$: (A) 55%, 1.25 x 10^5, ($[EtAlCl_2]_0$ = 2.0 mM); (B) 57%, 1.06 x 10^5; (C) 51%, 8.74 x 10^4; (D) 46%, 1.21 x 10^5. The concentrations of dioxane and $\bar{M}_w/\bar{M}_n$ ratios are as indicated.

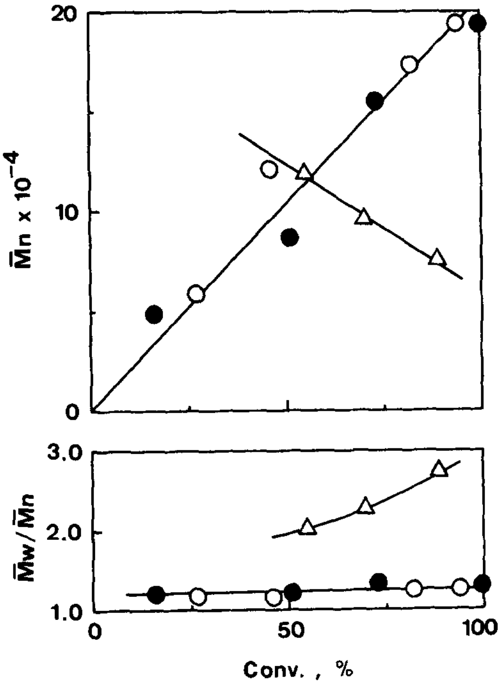


Figure 3. Relationships between monomer conversion and $\bar{M}_n$ or $\bar{M}_w/\bar{M}_n$ ratio for poly(IBVE) obtained with $EtAlCl_2$ in n-hexane at 0°C in the presence and absence of dioxane: $[IBVE]_0$ = 0.76 M (10 vol%); $[EtAlCl_2]_0$ = 20 mM. Dioxane in vol%: (△) none, ($[EtAlCl_2]_0$ = 2.0 mM); (●) 5.0; (○) 10.

proportionally to IBVE conversion, while the MWD remained narrow ($\bar{M}_w/\bar{M}_n$ = 1.1–1.3) throughout the reaction.

All these facts demonstrate that the IBVE polymerization with $EtAlCl_2$ in the presence of excess DO leads to living polymers with a narrow MWD.

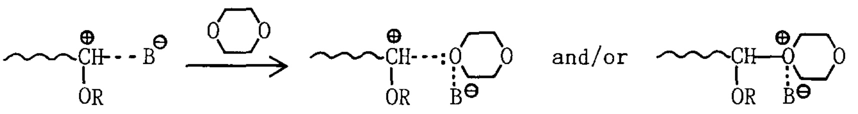
DISCUSSION

Intitiation

According to our separate experimemts (7), the IBVE polymerization with $EtAlCl_2$ in the presence of DO was accelerated by addition of a small amount of water (below the initial $EtAlCl_2$ concentration), and the $\bar{M}_n$ of the resulting polymers in turn decreased with increasing concentration of added water. Karl-Fisher titration indicated that the reaction mixtures with added DO contain 0.3–0.5 mM of adventitious water. Therefore, the true initiating entity in these reactions is most likely the proton derived from water and $EtAlCl_2$. In fact, as shown in Figure 3, the $\bar{M}_n$ of the polymers obtained in the presence of 5–10 vol% DO was ca. 2 x 10^5 (conversion = 100%), which in turn gives the living end concentration = 0.4 mM, close to the water concentration in the reaction mixture.

Propagating Species

Because the polymerization with $EtAlCl_2$ was living only when an excess amount of DO was present, the cyclic ether plays a crucial role in forming living polymers. Namely, the growing species of the type 1 (eq 1), being free from DO and consisting of the poly(IBVE) carbocation and the counteranion $B^{\ominus}$ derived from $EtAlCl_2$, can be neither stable nor living. We propose that DO may solvate the growing carbocation (as in 2) and/or may even form an oxonium ion 3 that is much more stable than the carbocationic species 1.



1 2 3 (1)

This hypothesis was supported by the fact that living polymerization of IBVE with $EtAlCl_2$ occurs in the presence of not only DO but also other ethers including diethyl ether (Et_2O) and tetrahydrofuran (THF) (7). Interestingly, the amount of the added ethers needed for living polymerization depended on their basicity; i.e., $Et_2O > DO > THF$.

Recently Mishra and Kennedy (8) have reported that tertiary ether/BCl_3 complexes induce living polymerization of isobutylene. These authors postulate that the growing end is stabilized by an alkoxyl group, complexed by BCl_3, which is derived from the tertiary ether. This stabilization mechanism totally differs from that (eq 1) for the living polymerization by our $EtAlCl_2$/dioxane system based on nucleophilic solvation.

The achievement of living polymerization with the $EtAlCl_2$/dioxane initiating system shows that not only a counteranion but also an externally added basic compound can prolong the lifetime of the propagating carbocation, provided that it interacts strongly with the active end. This lead gives us an important guideline to design new living cationic polymerization systems.

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