Polymer Bulletin 15, 417–423 (1986)

Polymer Bulletin

Living Cationic Polymerization of Vinyl Monomers by Organoaluminium Halides

1. $EtAlCl_2$/Ester Initiating Systems for Living Polymerization of Vinyl Ethers

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SUMMARY

Living cationic polymerization of isobutyl vinyl ether was achieved by $EtAlCl_2$ in the presence of ethyl acetate at rather high temperatures up to +25 °C in toluene. In the absence of the ester additives, neither living nor long-lived propagating species were formed under these conditions. Similarly, living propagating species of vinyl ethers with an ester unit in the pendant (2-vinyloxyethyl benzoate and methacrylate) were obtained with $EtAlCl_2$ alone. The obtained polymers showed a very narrow molecular weight distribution ($\overline{M}_w/\overline{M}_n<1.2$) and the $\overline{M}_n$ was directly proportional to the monomer conversion.

INTRODUCTION

Although a number of acidic compounds polymerize vinyl monomers, few afford truly living cationic polymerization. Perhaps the best initiator for this purpose is, thus far, a combination of hydrogen iodide and iodine (HI/I_2) that gives monodisperse living polymers from vinyl ethers and related monomers (1). Metal halides (MXn), which are usual initiators for cationic polymerization, lead to uncontrollable, transfer-dominant, non-living processes, except under special conditions (2-4). The most recent example of the formation of living-like species by MXn is the "quasi-living" polymerization developed by Kennedy et al. (4).

This series of studies is concerned with the living cationic polymerization of vinyl compounds initiated by metal halides modified with Lewis bases (e.g., esters), as a new class of cationic initiators that overcome the drawbacks of metal halides. In this study, we employed esters as a Lewis base modifier for ethylaluminum dichloride. These $EtAlCl_2$/ester initiating systems** eventually led to living cationic polymerization of vinyl ethers at rather high temperatures.

RESULTS AND DISCUSSION

Living Cationic Polymerization of IBVE by the $EtAlCl_2$/Ester Systems

Isobutyl vinyl ether (IBVE) was polymerized with $EtAlCl_2$ in the presence or absence of ethyl acetate or benzoate ($[ester]_0=[IBVE]_0=10$ vol%; $[EtAlCl_2]_0=20$ mM) in toluene at a low temperature (-40 °C). These esters are known to

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** Mixtures of an organoaluminium halide and an ester (or a carboxylic acid) have been used for cationic oligomerization (5,6) form complexes with MXn (7). All the polymerizations proceeded smoothly up to 100% conversion without an induction period. The additives remarkably retarded the polymerization; i.e., the half-life period of the monomer:

$$EtAlCl_2 \text{ (0.1 hr)} < EtAlCl_2 + \text{ethyl benzoate (6.5 hr)} < EtAlCl_2 + \text{ethyl acetate (27 hr)}.$$

Figure 1 shows the molecular weight distribution (MWD) of the polymers obtained at high conversions (>85 %). The dependence of their number-average molecular weights ($\bar{M}_n$) on conversion is shown in Figure 2. EtAlCl2 alone, similarly to BF_3OEt_2, gave high polymers ($\bar{M}_n \sim 10^5$) with a broad MWD ($\bar{M}_w/\bar{M}_n > 2$); the $\bar{M}_n$ decreased slightly with conversion. On the other hand, the MWDs with both $EtAlCl_2$/ester systems were narrower, obviously shifting toward higher molecular weight as the polymerization proceeded. Ethyl acetate affected the polymer molecular weight, MWD, and polymerization rate much greater than ethyl benzoate. In particular, the acetate ester led to quite narrow MWD with $\bar{M}_w/\bar{M}_n = 1.1 - 1.3$.

The $\bar{M}_n$ of the polymers obtained with the $EtAlCl_2$/ester systems was proportional to conversion (Fig. 2). This, coupled with the narrow MWD, shows that living polymers are formed from IBVE by $EtAlCl_2$ in conjunction with esters. It is the first time that a living cationic polymerization has been achieved with typical metal halides.

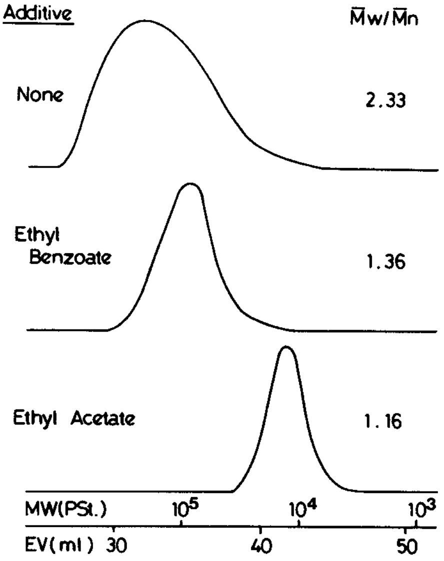

Figure 1. MWD of poly(IBVE) obtained by $EtAlCl_2$ in the presence and absence of esters in toluene at -40°C: $[IBVE]_0$ = 10 vol% (0.76 M), $[EtAlCl_2]_0$ = 20 mM, $[ester]_0$ = 10 vol%. Ester additives and $\bar{M}_w/\bar{M}_n$ as indicated.

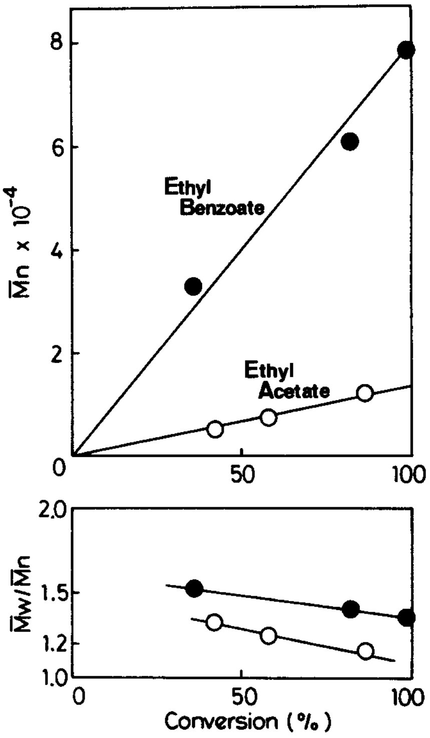

Figure 2. Relationships between conversion and $\bar{M}_n$ or $\bar{M}_w/\bar{M}_n$ ratio for poly(IBVE) obtained with $EtAlCl_2$ in the presence of esters at -40°C: $[IBVE]_0$=10 vol% (0.76 M), $[EtAlCl_2]_0$=20 mM, $[ester]_0$=10 vol%. Additive:(●)ethyl benzoate;(○)ethyl acetate.

The IBVE polymerizations at different $EtAlCl_2$/ester molar ratios indicated that the esters should be added in excess over $EtAlCl_2$ to realize living propagation. For example, when an equimolar mixture of $EtAlCl_2$ and ethyl acetate or benzoate was used, the obtained polymers exhibited a broad MWD ($\overline{M}_w/\overline{M}_n$>2) and $\overline{M}_n$'s unchanged with conversion. The polymerization rate, however, was smaller than that with $EtAlCl_2$ alone.

Living Polymerization at Higher Temperature

The living cationic polymerization of vinyl ether was found to be possible at such a low temperature (-40 °C), although the rate of polymerization was very low. In order to elucidate the effect of temperature on the "long-lived" nature of propagating species and to increase the reaction rate, polymerizations were carried out at relatively high temperature.

Figure 3 shows the effect of temperature on the time-conversion curves for the polymerization of IBVE by the $EtAlCl_2$/CH_3COOEt system in toluene. The polymerization at +25 °C was rapid and completed within 2 hr, whereas at -40 °C it took about one week to reach ca. 90% conversion.

At -15 °C or above, the polymerization mixture with the $EtAlCl_2$/CH_3COOEt system was colorless, whereas in the absence of the ester component, it intensely colored (green to dark violet). The strong color in the latter indicates the extensive occurrence of chain transfer, leading to conjugated olefin terminals (8).

Rather surprisingly, the polymerizations by the $EtAlCl_2$/CH_3COOEt system remained "living" even at higher temperatures up to +25 °C, as shown in Figures 4 and 5. The polymers obtained in the temperature range -15° - +25 °C (Figure 4) all exhibited very narrow MWDs ($\overline{M}_w/\overline{M}_n$ =1.12-1.15) without tailing. Their $\overline{M}_n$'s were directly proportional to conversion, irrespective of the change of polymerization temperatures (Figure 5). Over the whole range of conversion, the $\overline{M}_w/\overline{M}_n$ ratio stayed below 1.2, slightly decreasing at higher conversions. All these results confirm the living nature of the polymerizations.

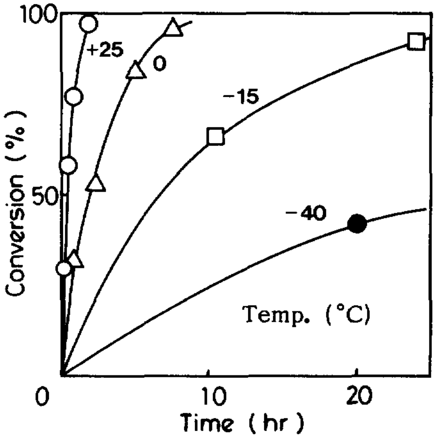

Figure 3. Effect of temperature on the time-conversion curves for the polymerization of IBVE by the $EtAlCl_2$/CH_3COOEt system in toluene:$[IBVE]_0$=10 vol% (0.76M), $[EtAlCl_2]_0$=20 mM, $[CH_3COOEt]_0$= 10 vol%. Temperatures as indicated.

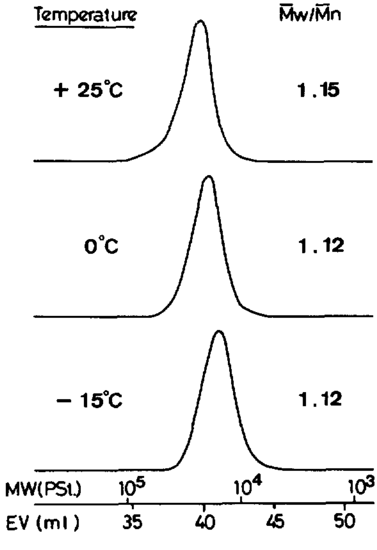

Figure 4. Effect of temperature on the MWD of poly(IBVE) obtained by the $EtAlCl_2$/CH_3COOEt system in toluene: $[IBVE]_0$=10 vol% (0.76 M), $[EtAlCl_2]_0$ =20 mM, $[CH_3COOEt]_0$=10 vol%; conversion > 90%. Temperatures and $\overline{M}_w/\overline{M}_n$ as indicated.

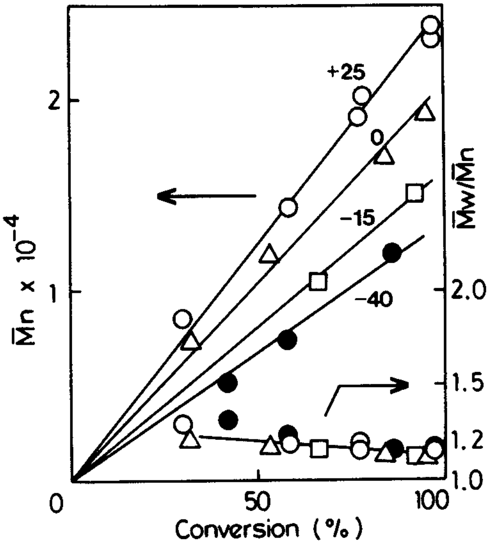

Figure 5. Effect of temperature on relationships between conversion and $\overline{M}_n$ or $\overline{M}_w/\overline{M}_n$ ratio in the polymerization of IBVE by the $EtAlCl_2$/ CH_3COOEt system in toluene: $[IBVE]_0$=10 vol% (0.76 M), $[EtAlCl_2]_0$=20 mM, $[CH_3COOEt]_0$=10 vol%. Temperature: (○)+25 °C; (△)0 °C; (□)-15 °C; (●)-40 °C.

Further inspection of Figure 5 shows that the polymer molecular weight is higher at higher temperatures, a trend quite opposite to that in conventional (transfer-dominant) cationic polymerization. In fact, the number of polymer chains produced per initiator ($EtAlCl_2$), calculated from the linear $\overline{M}_n$-conversion plots, decreased at higher temperatures (-15 °C, 0.24; 0 °C, 0.18; +25 °C, 0.15), while remained almost constant during the course of polymerization. Thus, in the $EtAlCl_2/CH_3COOEt$-initiated polymerization, chain transfer is essentially absent even at temperatures as high as +25 °C, although the initiation efficiency is not so high.

According to structural analysis of the polymers by ^{1}H and ^{13}C NMR spectroscopy, the IBVE polymerization by $EtAlCl_2/CH_3COOEt$ proceeds without any side reactions; the polymers were free of ester groups derived from CH_3COOEt, neither complexing nor bonded chemically. Their steric structure was almost the same as that obtained with $EtAlCl_2$ alone, consisting of 70% meso and 30% racemic diads.

Living Cationic Polymerization of Vinyl Ethers with an Ester Pendant

The successful living polymerization of IBVE by $EtAlCl_2$ in the presence of esters prompted us to polymerize vinyl ethers with an ester pendant using $EtAlCl_2$ alone as initiator. 2-Vinyloxyethyl benzoate (VEBz) and 2-vinyloxyethyl methacrylate (VEM) were employed as such vinyl ethers. In these cases, an ester modifier for the metal halide is "internally" incorporated in the monomer, rather than "externally" added as in the polymerization by the $EtAlCl_2$/ester systems. Note that VEBz, an aromatic ester, is similar in structure to ethyl benzoate, whereas VEM, an unsaturated aliphatic ester, to ethyl acetate. We have already reported the living cationic polymerizations of these vinyl ethers initiated by HI/I_2 at low temperatures (9,10).

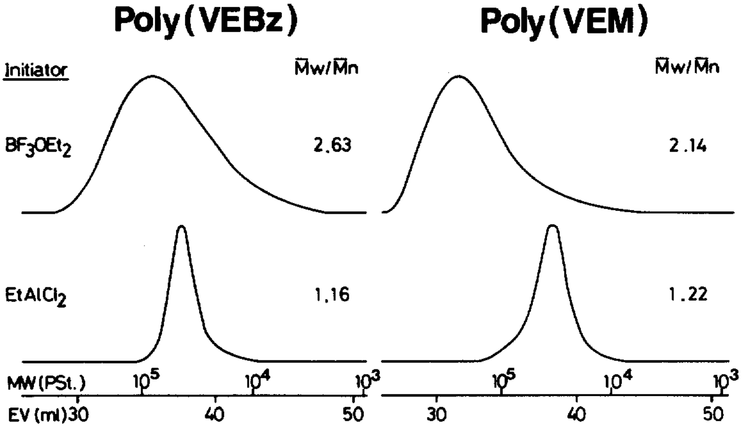

Figure 6. MWDs of poly(VEBz) and poly(VEM) obtained with $EtAlCl_2$ and BF_3OEt_2 (no ester additives) in toluene at -15 °C: $[VEBz]_0$=0.56 M; $[VEM]_0$=0.64 M; $[Initiator]_0$=20 mM.

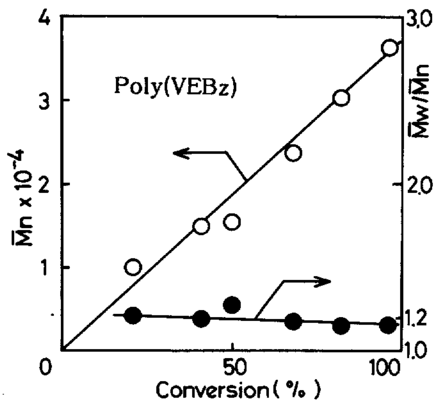

Figure 7. Relationships between conversion and $\bar{M}_n$ (○) or $\bar{M}_w/\bar{M}_n$ ratio (●) in the polymerization of VEBz by $EtAlCl_2$ in toluene at -15 °C; $[VEBz]_0$=0.56 M, $[EtAlCl_2]_0$=20 mM.

Figure 6 shows the MWD of the polymers of VEBz and VEM produced by $EtAlCl_2$ (and BF_3OEt_2 for comparison) in toluene at -15 °C. Very narrow MWDs ($\bar{M}_w/\bar{M}_n$ ~1.2) were obtained by $EtAlCl_2$, in contrast to the broad MWDs by BF_3OEt_2. The conversion dependence of the $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of poly(VEBz) obtained with $EtAlCl_2$ is shown in Figure 7. The $\bar{M}_n$ increased proportionally to conversion. The MWD of the produced polymers remained very narrow ($\bar{M}_w/\bar{M}_n$ ~1.2) at any conversion. Thus, $EtAlCl_2$ alone induced living polymerization of the ester-containing vinyl ethers.

In conclusion, this work has shown that $EtAlCl_2$, in the presence of esters both as additives and as pendant groups in the monomer, initiates living polymerization of vinyl ethers in toluene, to give high molecular weight polymers with a very narrow MWD ($\bar{M}_n > 10^4$, $\bar{M}_w/\bar{M}_n \leq 1.2$). It is of interest that this living polymerization can be carried out at relatively high temperatures (-15 °C to +25 °C) where cationic polymerization of vinyl compounds cannot generally give high polymers.

Further kinetic and mechanistic studies are now in progress.

EXPERIMENTAL

Materials

Commercial IBVE was washed with an aqueous alkaline solution and then with water. VEBz and VEM were prepared by the reactions of 2-chloroethyl vinyl ether with sodium benzoate and methacrylate, respectively (10). The three monomers were distilled twice over calcium hydride before use. $EtAlCl_2$ was commercially obtained as an n-hexane solution (Kanto Chemicals) or an n-heptane solution (Japan Alkyl Aluminium Co.) and used without further purification. BF_3OEt_2 was purified by distillation under reduced pressure. Ethyl acetate and benzoate (Wako Chemicals, both guaranteed reagents) were distilled over magnesium sulfate and calcium hydride, respectively. Toluene was purified by the usual methods and distilled over calcium hydride at least twice before use.

Procedures

Polymerization was carried out 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 into a monomer solution, and quenched with ammoniacal methanol. The ester additives, when employed for IBVE polymerization, were added to a monomer solution before the addition of $EtAlCl_2$. The quenched reaction mixture was sequentially washed with a dilute aqueous acid and water to remove the initiator residues, and the products were recovered by evaporating the organic layer under reduced pressure.

The MWD of the polymers was measured by size-exclusion chromatography (SEC) using polystyrene gel columns (1). The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ ratios were calculated from SEC curves on the basis of a polystyrene caribration. ^1H and ^{13}C NMR spectra (89.55 and 22.5 MHz, respectively) were recorded on a JOEL FX-90Q spectrometer in $CDCl_3$. The steric structure of the polymers was determined by ^{13}C NMR spectroscopy (11).

Acknowledgement. We thank Dr. M. Sawamoto of this laboratory for his helpful discussion.

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Accepted May 14, 1986 *S*