

Living Cationic Polymerization of Vinyl Monomers by Organoaluminum Halides V. Polymerization of Isobutyl Vinyl Ether with EtAlCl₂ in the Presence of 2,6-Dimethylpyridine and Related Amines

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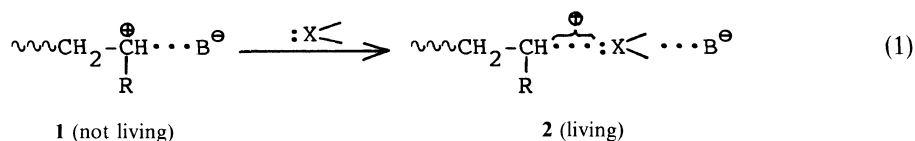
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ABSTRACT: In the presence of 2,6-dimethylpyridine as an added base, living cationic polymerization of isobutyl vinyl ether was achieved in *n*-hexane at 0 to +40°C with the 1-(isobutoxy)ethyl acetate (**3**)/ethylaluminum dichloride [CH₃CH(O*i*Bu)-OCOCH₃/EtAlCl₂] initiating system. A low concentration of the pyridine, 4 times that of the cationogen **3** (or the active end), was sufficient for the living process. Without the added amine, the polymerization was almost instantaneous and nonliving. The use of triethylamine and less hindered pyridines (pyridine, 2-methylpyridine, and 2,4-dimethylpyridine), in place of the 2,6-dimethyl derivative, failed to induce living polymerization but instead resulted in chain termination. In contrast, highly crowded 2,3-di-*t*-butylpyridine could not affect the polymerization by **3**/EtAlCl₂ at all. It is proposed that 2,6-dimethylpyridine stabilizes the otherwise unstable growing carbocation *via* a nucleophilic interaction to endow it with livingness. The effects of the pyridine structures showed not the basicity but the steric crowding around the nitrogen to play a critical role in the nucleophilic stabilization of the growing cation.

KEY WORDS Living Polymerization / Cationic Polymerization / Carbocation Stabilization / Amine / 2,6-Dimethylpyridine / Isobutyl Vinyl Ether / Ethylaluminum Dichloride /

For living cationic polymerization of vinyl monomers, we have recently proposed the concept, "stabilization of propagating carbocations by added bases" (eq. 1),¹ *i.e.*, the use of externally added basic compounds (:X⁻) that stabilize an unstable nonliving growing cations

(**1**) through nucleophilic interaction and thereby eliminate chain transfer, termination, and other undesirable side reactions to form a living species (**2**); B[⊖] represents a weakly nucleophilic counteranion derived from a metal halide:



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and, if it proves feasible, (2) which amines as well as reaction conditions are most suitable.

EXPERIMENTAL

Materials

Commercial IBVE (Tokyo Kasei) was washed with an aqueous alkaline solution and water, and distilled twice over calcium hydride just before use. EtAlCl_2 was commercially obtained as an *n*-hexane solution (1.0 M; Kanto Chemicals) and used without further purification. Triethylamine (Et_3N), pyridine (Py), 2-methylpyridine, 2,4-dimethylpyridine, 2,6-dimethylpyridine (DMePy), and 2,6-di-*t*-butylpyridine (DtBuPy) (all guaranteed reagents) were dried over Drierite (CaSO_4) and distilled twice over calcium hydride or lithium aluminum hydride before use. *n*-Hexane as a solvent was purified by the usual method and distilled at least twice over calcium hydride just before use.

1-(Isobutoxy)ethyl acetate (**3**) was prepared from IBVE and acetic acid, as previously reported³, and distilled twice over calcium hydride under reduced pressure.

Procedures

Polymerization was carried out at 0—+70°C under a dry nitrogen atmosphere in a baked glass tube equipped with a three-way stopcock. To a mixture of IBVE, an amine additive, and cationogen **3** in *n*-hexane kept at -78°C was added an *n*-hexane solution of EtAlCl_2 . The mixture was vigorously stirred manually at -78°C and then brought to the reaction temperature so as to initiate the polymerization (see the text). After a predetermined interval the polymerization was quenched with ammoniacal methanol. The quenched reaction mixture was washed with dilute hydrochloric acid (*ca.* 1N) and then with water to remove the initiator residues, neutralized with a dilute aqueous sodium hydroxide solution, evaporated under reduced pressure, and vacuum dried overnight to recover the

product polymers. 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 (SEC) in chloroform at room temperature on a Jasco Trirotar-II instrument equipped with three polystyrene gel columns (Shodex K-802, 803, and 804; 8.0 i.d. × 300 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.





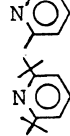
RESULTS AND DISCUSSION

Selection of Amines

The primary phase of this study was directed to determine the effects of added amines on the polymerization of IBVE initiated by the $3/\text{EtAlCl}_2$ system in *n*-hexane at 0°C (*cf.* Scheme 1). The added amines included an aliphatic amine (Et_3N) and a series of pyridine derivatives with an alkyl substituent(s) and, in view of their high basicity, the amounts of the additives were each set at 20 mM, 4-fold molar excess over the cationogen **3** but less than 1/50 of those for the ester or ether counterparts employed in our previous studies.²⁻⁵ Table I summarises the overall results of these first-phase experiments in terms of the time course of the polymerizations and the yield and MWD of the produced polymers.

The polymerization carried out in the absence of an amine was very rapid (100% IBVE conversion within 1 min) and not living.³ Consistent with the earlier observations,^{6,7} the use of Et_3N , pyridine, 2-methylpyridine, and 2,4-dimethylpyridine resulted in incomplete polymerizations that consisted of a rapid initial phase followed by a plateau region where conversion no longer increased. Evidently, these amines induced chain termination reactions. In contrast, DtBuPy apparently had no effects at all; even when its concentration was raised 50 times to 1.0 M, the polymerization was virtually identical in rate and prod-

Table I. The Effects of Various Amines on the IBVE Polymerization by 3/EtAlCl₂^a

Amine	pK _a ^b	Polymerization	Final conv./%	\bar{M}_n	\bar{M}_w/\bar{M}_n
None	—	rapid, quantitative	100	17100	2.64
(C ₂ H ₅) ₃ N(Et ₃ N)	10.8 ^c	incomplete (termination)	~5	2500	3.86
 (Py)	5.21	incomplete (termination)	~15	9000	2.93
	5.94	incomplete (termination)	~5	11000	3.76 ^e
	6.77	incomplete (termination)	~5	9300	4.88 ^e
 (DMePy)	6.60	slow, quantitative	70 ^d	16000	1.44
 (DtBuPy)	n.d.	rapid, quantitative	100	23600	2.70

^a [IBVE]₀ = 0.76 M; [EtAlCl₂]₀ = 20 mM; [3]₀ = 4.0 mM; [Amine] = 20 mM; in *n*-hexane at 0°C. *ca.* 30 h.

^b In water at +25°C; concentration of an amine = 0.005 M. Reference 9.

^c Reference 10.

^d Reaction time = *ca.* 200 h.

^e Bimodal MWD.

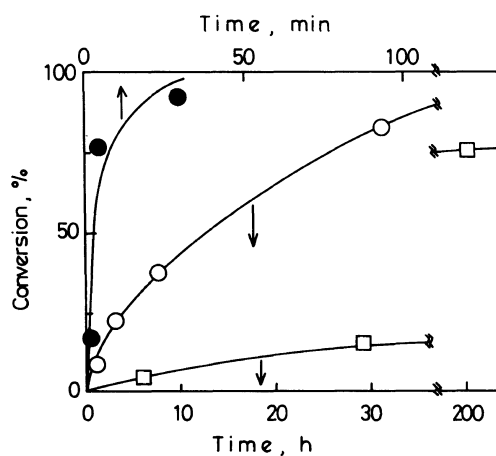


Figure 1. Time-conversion curves for the IBVE polymerization by 3/EtAlCl₂ in *n*-hexane in the presence of DMePy: [IBVE]₀ = 0.76 M; [EtAlCl₂]₀ = 20 mM; [3]₀ = 4.0 mM. [DMePy] and temperature: (□) 20 mM, 0°C; (○) 10 mM, 0°C; (●) 10 mM, +40°C.

uct to that without an added amine.

The most interesting result was obtained for DMePy, which carries two methyl groups on both sides of the nitrogen. The polymerization

in the presence of this disubstituted pyridine was much slower than in its absence, but it proceeded smoothly without an induction period up to high conversion (70% in 200 h; see also Figure 1).

In addition to the time-conversion relationships, the MWD of the product polymers was found to be affected as well by the added nitrogen bases. For example, the amines (Et₃N, pyridine, 2-methylpyridine, and 2,4-dimethylpyridine) that induced termination all led to broadening of the MWD from $\bar{M}_w/\bar{M}_n = 2.6-2.7$ to 3-5. In sharp contrast, DMePy alone gives polymers with a clearly narrower MWD ($\bar{M}_w/\bar{M}_n = 1.44$).

These results suggest the formation of a long-lived propagating species in the presence of DMePy. It is also of interest that the trends seen in Table I cannot be accounted for by the difference in the amine basicity (see the pK_a values in Table I⁹); note, in particular, the similarity of the results obtained with Et₃N and Py, the most and least basic, respectively, among the six amines employed. The data for

the series of pyridines instead show steric crowding around the nitrogen atom to play a critical role in the interaction of the amines with the propagating carbocations (see the last section of this paper below). Thus, we decided to use DMePy as the amine additive in the second-phase study for further search of living cationic polymerization.

Polymerization in the Presence of DMePy

Figures 1 and 2 show, respectively, the time- and \bar{M}_n -conversion plots for the IBVE polymerization by the 3/EtAlCl₂ initiating system in *n*-hexane at 0 and +40°C in the presence of DMePy (10–20 mM). At both temperatures, the polymerizations were quantitative, free from an induction phase, and invariably much slower than in the absence of the pyridine; the higher the DMePy concentration, slower the polymerization (Figure 1).

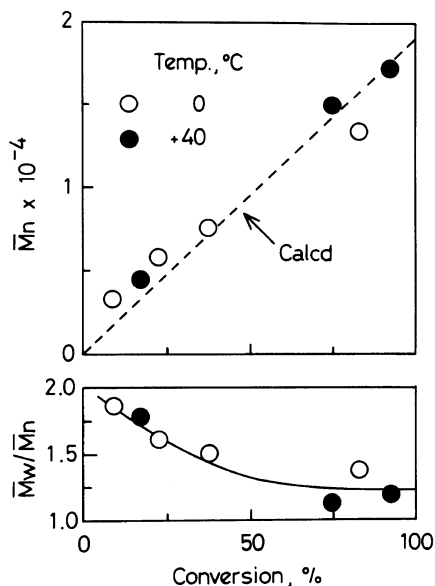


Figure 2. Relationships between conversion and \bar{M}_n or \bar{M}_w/\bar{M}_n ratio for the IBVE polymerization by 3/EtAlCl₂ in *n*-hexane in the presence of DMePy: [IBVE]₀ = 0.76 M; [EtAlCl₂]₀ = 20 mM; [3]₀ = 4.0 mM; [DMePy] = 10 mM. Temperature: (○) 0°C; (●) +40°C. The diagonal broken line indicates the calculated \bar{M}_n value assuming the formation of one polymer chain per molecule of 3.

Of interest is that even at +40°C the \bar{M}_n of the polymers was directly proportional to monomer conversion and in good agreement with the calculated value assuming that one polymer chain forms per molecule of the cationogen 3 (the diagonal broken line in Figure 2). The polymer MWDs ($\bar{M}_w/\bar{M}_n = 1.2$ –1.8) were broader than a monodisperse distribution, but considerably narrower than those without an amine additive ($\bar{M}_w/\bar{M}_n = 2.64$) and progressively narrowed with increasing conversion. Thus, the presence of DMePy permits the formation of a long-lived propagating species (the proportionality of \bar{M}_n to conversion), although the initiation is slower than the propagation (the MWD not monodisperse and narrowing along with the progress of the polymerization). Experiments carried out at +70°C but otherwise the same as above failed to increase polymer molecular weight with conversion, indicating that the highest temperature for the generation of the long-lived intermediate is below this level.

The long lifetime of the growing species in the presence of DMePy was further demonstrated by sequential addition of fresh IBVE feeds to polymerized reaction mixtures at

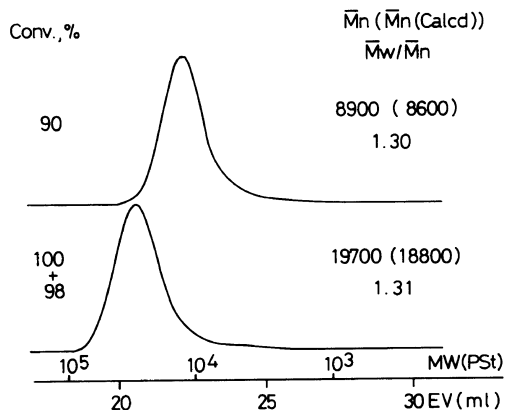


Figure 3. MWD of poly(IBVE) obtained in a monomer-addition experiment in the IBVE polymerization by 3/EtAlCl₂ in the presence of DMePy in *n*-hexane at +40°C: [IBVE]₀ = 0.38 + 0.38 M; [EtAlCl₂]₀ = 20 mM; [3]₀ = 4.0 mM; [DMePy] = 10 mM.

+40°C (“monomer-addition” experiments). Upon addition of an IBVE feed, a second-stage polymerization smoothly ensued which was again near quantitative. As Figure 3 shows, the MWD of the products after the monomer addition remained as narrow as that for the first-stage process, and it clearly shifted toward higher molecular weight with the progress of the polymerization. The polymer \bar{M}_n s accordingly increased in direct proportion

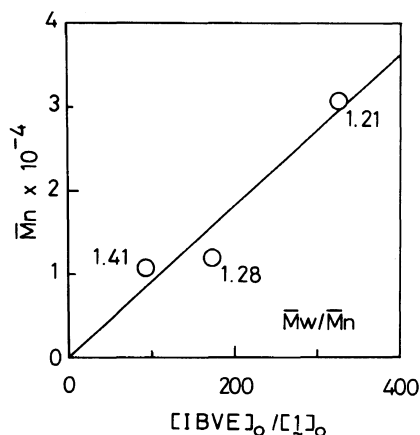


Figure 4. \bar{M}_n values of poly(IBVE) obtained by 3/EtAlCl₂ in *n*-hexane at 0°C in the presence of DMePy as a function of the [IBVE]₀/[living end] ratio: [IBVE]₀ = 0.76 M; [EtAlCl₂]₀ = 20 mM; [3]₀ = 2.0, 4.0, or 8.0 mM; [DMePy] = 10 mM.

to monomer conversion and were close to the calculated values (one polymer chain per molecule of 3). Separate experiments revealed that the \bar{M}_n values for 100% IBVE conversion are inversely proportional to the initial concentration of 3 but independent of those of EtAlCl₂ and DMePy; see Figure 4 for a typical example of such dependence.

Thus, a living polymerization of IBVE by the 3/EtAlCl₂ was achieved at temperatures below +40°C in the presence of a small amount of the pyridine.

Effects of Polymerization Procedures

The polymerization experiments described above were all performed by mixing all the ingredients (IBVE, 3, EtAlCl₂, DMePy, and *n*-hexane) at -78°C where progress of the reaction could safely be ignored. The thoroughly stirred mixture was then transferred to a bath maintained at 0 or +40°C to commence the polymerization that gives living polymers with narrow MWDs (Figure 5B). Although in the routine experiments EtAlCl₂ was invariably the last component to be added to a polymerization solution, the order of reagent addition did not affect the results at all, as long as the mixing was through and carried out at -78°C.

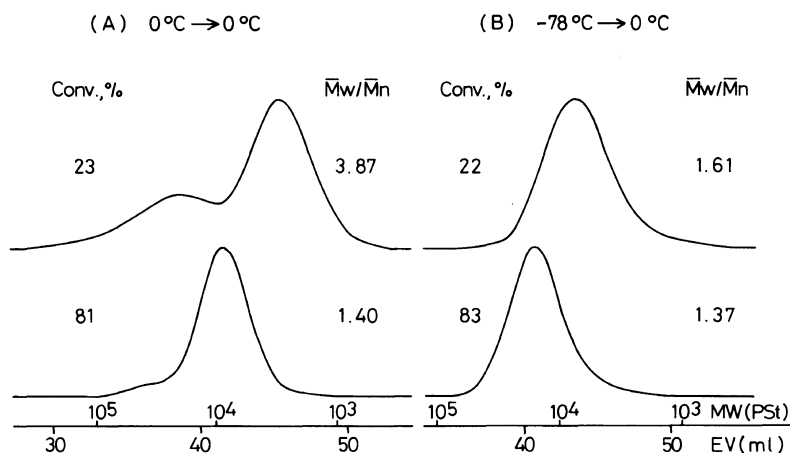


Figure 5. MWD of poly(IBVE) obtained with 3/EtAlCl₂ in *n*-hexane at 0°C in the presence of DMePy: Effects of the temperature of EtAlCl₂ addition (A, 0°C; B, -78°C). [IBVE]₀ = 0.76 M; [EtAlCl₂]₀ = 20 mM; [3]₀ = 4.0 mM; [DMePy] = 10 mM.

Rather by accident, we found the MWD of polymers to depend on the temperature at which EtAlCl_2 is added to a polymerization solution. For example, when the Lewis acid was brought in contact with an IBVE/3/DMePy mixture at 0°C , the polymerization proceeded at the same temperature at a rate very similar to that with the mixing of EtAlCl_2 at -78°C , but the resultant polymers turned out to exhibit bimodal MWD (Figure 5A).

The lower polymer fraction is similar in MWD and molecular weight to the living polymers shown in Figure 5B and has a long lifetime, as indicated by the increase in its molecular weight with increasing conversion. The higher polymer fraction, on the other hand, is broadly distributed and apparently not living, without a noticeable molecular weight increase. As the polymerization proceeded, the amount of this nonliving fraction decreased relative to the long-lived lower polymer, and hence the higher was predominantly formed during the early stages of the reaction.

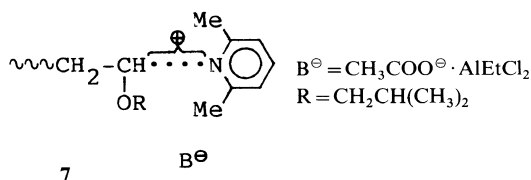
Thus, when EtAlCl_2 is mixed at 0°C , the early stages of the polymerization involve two parallel propagation steps, one being living and the other nonliving. The lack of livingness of the latter in turn indicates the absence of the intervention of added DMePy therein, and the nonliving propagation is most likely mediated by the unstable species **5** (Scheme 1) that is free from the pyridine's nucleophilic interaction (*cf.* eq. 1). Because of its low concentration, DMePy would need some time to establish the interaction with the growing carbocation (**5**); at 0°C the propagation *via* **5** is too fast to be completely suppressed by the added amine, at least during the initial phase of the polymerization.

It is therefore recommended that the living polymerization by the **5**/ EtAlCl_2 in the presence of a small amount of DMePy (or other bases of similar nature) be carried out by thoroughly mixing all the ingredients at -78°C . In contrast, such precautions are

unnecessary for the corresponding living processes using esters and ethers as added bases,²⁻⁵ whose concentrations (*ca.* 1 M) are usually much higher than that of DMePy and thereby allow the bases to interact with the growing cation rapidly even at 0°C so as to eliminate the nonliving propagation via **5** completely.

CONCLUSIONS

This study has shown that DMePy is effective as an nitrogen base for stabilizing the unstable growing carbocation **5** to permit living polymerization of IBVE by the 3/ EtAlCl_2 initiating system. The carbocation stabilization apparently involves a nucleophilic interaction of the pyridine with the cationic site of **5**; and we propose the structure **7** for the possible form of the amine-stabilized living species, which is similar to **6** with an ester or ether (Scheme 1).



A feature of the use of the pyridine is that a low concentration, below 1/50 those for the oxygen bases,²⁻⁵ is sufficient for effective stabilization, which effectiveness is consistent with the higher nucleophilicity of the nitrogen bases.

As already pointed out (see Table I), the interaction of pyridines with carbocations does not simply depend on their basicity (proton affinity; represented by $\text{p}K_a$) but instead on the steric environment around the nitrogen atom. The termination reaction induced by Py implies that its nitrogen, through conjugated with the aromatic system, is still nucleophilic enough to form a stable pyridinium cation incapable of propagation.⁶ The two *ortho* methyl groups in DMePy sterically prevent the

formation of such a carbon–nitrogen bond, while permitting a suitably strong nucleophilic interaction of the nitrogen with the growing cation and in turn the formation of the living species 7. Note that nitrogen of DMePy is *per se* more basic than that of Py, as evidenced by their pK_a values (DMePy > Py; Table I). For DtBuPy, however, the steric effect of the two bulky *t*-butyl substituents overrides the nitrogens' nucleophilicity, rendering this crowded derivative completely ineffective in carbocation stabilization.

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