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Communications to the Editor

Nature of Active Species in the Living Cationic Polymerization of Vinyl Ethers Initiated by HX/Zinc Halide Systems

We have recently reported[1] that vinyl ethers are able to polymerize by a living mechanism, when HCl or HBr is used as a substitute for HI in HI/Lewis acid initiating systems.[2] Kinetics of the chloroethyl vinyl ether (CEVE) polymerization performed under constant experimental conditions, in the presence of zinc halides, give the following reactivity order, for the various halide end groups:

$$\text{-CHORI} \geq \text{-CHORBr} \gg \text{-CHORCl}$$

Despite the large difference in the polymerization rates, according to the nature of the halogen termini, as shown in Figure 1, all these initiating systems including the chloride one result in complete consumption of the initiator and lead to poly(chloroalkyl vinyl ethers) with theoretically predicted $\bar{M}_n$ and narrow MWD; typical GPC traces of the poly(CEVE) obtained with Cl and I termini are given in Figure 2 (I and II).

In the present study, the difference in polymerization rates between the chloro- and iodo-based systems has been used to investigate the nature of propagating species in the living polymerization of vinyl ethers initiated by combinations of a Brönsted acid (HX) and a Lewis acid (ZnX_2).

There is a general agreement on an activation of the carbon–halogen terminal bonds involving a dynamic and reversible interaction of the halogen atom with a Lewis acid molecule of the system.[2] In other words, a chain end is active part of the time and inactive another part.

Various types of active species, i.e., covalent[3] or ionic ones,[4] have been speculated to account for the living character of the polymerizations.

Higashimura and co-workers[3] first proposed an insertion of the monomer into an activated covalent end group, via a multicenter rearrangement mechanism, as illustrated in Chart I.

Besides, a temporary ionization of the terminal carbon–halogen bond, assisted by the Lewis acid, has also recently been suggested,[4] taking solvent polarity and the effect of other reaction parameters into account.

According to the first reaction pathway—a covalent mechanism in living polymerization conditions—the covalently linked terminal halogen should remain attached to the same polymer chain from the early stages to the end of the propagation step. Initiation of the polymerization by a mixture of chloro and iodo derivatives would result in a system in which chains grow at different rates, thus leading to bimodal MWD.

Elsewhere, in the case of an activation mechanism involving the formation of ionic species, rapid exchange between chloride and iodide counterions would occur among growth species; this would result in the formation of monomodal MWD, regardless of the nature of the initial halogen group attached to the chain.

The two different reaction pathways are illustrated in Schemes I and II.

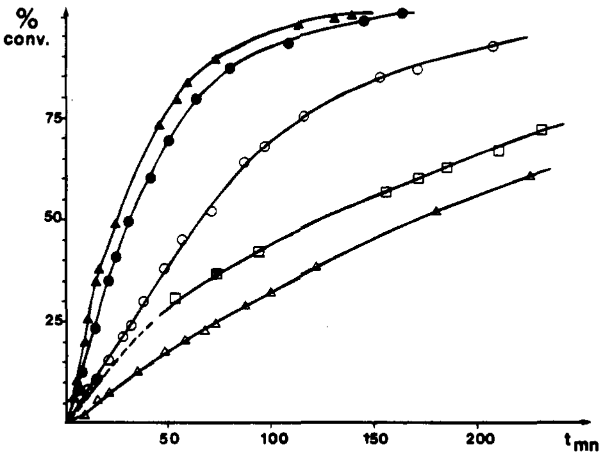


Figure 1. Time–conversion curves for the polymerization of CEVE initiated by various initiating systems in CH_2Cl_2 at −30 °C: (▲) $-CH(OR)I/ZnCl_2$; (△) $-CH(OR)Cl/ZnCl_2$; (●) $-CH(OR)Cl$ + $-CH(OR)I$ (1:3)/$ZnCl_2$; (○) $-CH(OR)Cl$ + $-CH(OR)I$ (3:1)/$ZnCl_2$; (□) $-CH(OR)Cl$ + $-CH(OR)I$ (5:1)/$ZnCl_2$; [initiator] = 3.2×10^{-3} M; [initiator]/[$ZnCl_2$] = 10.5; [CEVE] = 3 M.

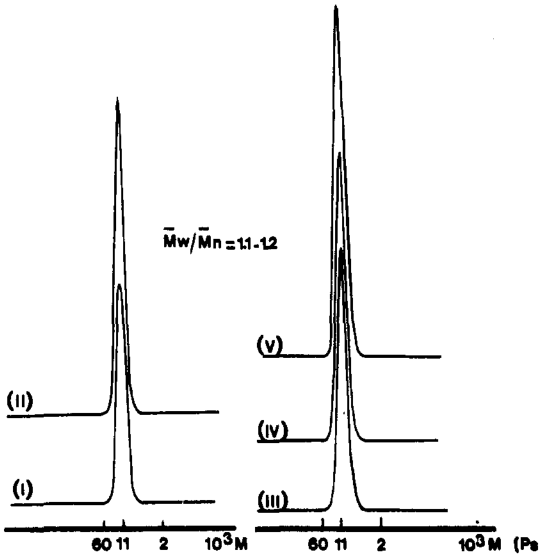
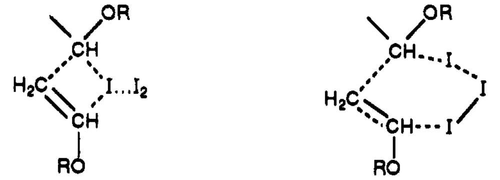


Figure 2. GPC chromatograms of poly(CEVE) obtained from different initiating systems based on HI, 1-chloroethyl 2-chloroethyl ether (RCl), and their mixtures (see Figure 1) and after complete monomer conversion: (I) HI; (II) RCl; (III) RCl/HI = 1/3; (IV) RCl/HI = 3/1; (V) RCl/HI = 5/1.

Chart I



4-membered transition state (3) 6-membered transition state (5)

In order to characterize the operative polymerization pathway, the kinetics of CEVE polymerization initiated by the chloride and iodide adducts of CEVE and by their (5:1)(3:1) and (1:3) mixtures, in the presence of zinc chloride

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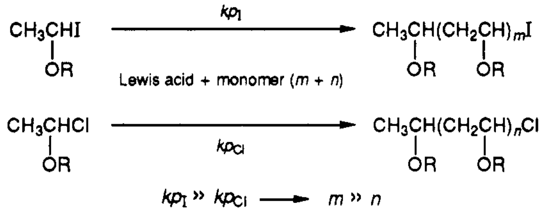
Table I
Polymerization of CEVE Initiated by HCl and HI Vinyl Ether Adducts and Their Mixtures, with Zinc Halides as Catalyst (Solvent CH_2Cl_2, $T = -30$ °C, $[M]_0 \simeq 3$ M, $[ZnCl_2] = 3.2 \times 10^{-3}$ M)

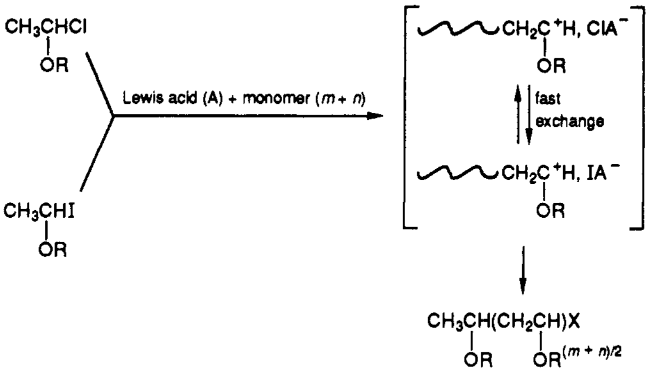
initiators, 10^{-3} M					$\bar{M}_n$[d]		
R^bI	R^bCl	$t_{50\%}$, min	10^4R_p, M s^{-1}	10^3R_p/([RI] + [RCl])M, M^{-1} s^{-1}	theor[c]	exptl[d]	I
0	32	170	1.7	1.8	9900	12000	1.15
5.4	27	130	2.6	2.7	9900	9300	1.15
5.4[a]	27				9900	8800	1.16
9	23	65	3.8	3.7	9900	9600	1.20
28	7	32	8.3	7.9	9800	9100	1.20
32.3	0	25	11.4	11.7	9900	10700	1.17

[a] ZnI_2 as catalyst. [b] R = $CH_3CHO(CH_2)_2Cl$. [c] Calculated from the equation $\bar{M}_n$(theor) = ([CEVE]$_0$/([RI] + [RCl]))M_{CEVE}. [d] Determined at the end of polymerizations after complete monomer conversion.

Scheme I
Polymerization via Insertion into Activated Covalent Bonds



Scheme II[a]
Polymerization Involving Ionic Active Species



[a] X = Cl, I.

as catalyst, has been examined. Kinetics curves obtained in CH_2Cl_2, at −30 °C, are shown in Figure 1.

With the iodo end group, 50% monomer conversion is reached within 25 min whereas $t_{50\%}$ is about 170 min with the chloro terminal group. Mixtures of the two adducts exhibit intermediate reactivities depending on their respective composition (see Table I). Assuming the following simplified kinetic equation

$$R_p(\text{app}) = -\frac{dM}{dt} = k_p(\text{app})[RX][M]$$

for similar polymerization conditions, apparent polymerization rates have been calculated from the monomer versus time curves, determined by dilatometry (Figure 1). Results are collected in Table I.

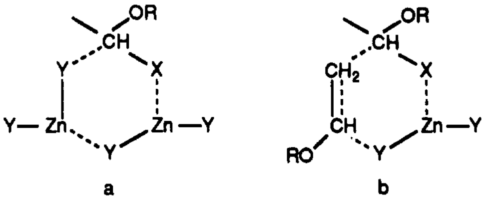
GPC chromatograms of the poly(CEVE) obtained with different initiator compositions are shown in Figure 2. The good agreement between the molar masses of poly(CEVE)s determined by tonometry and by GPC on the basis of a polystyrene calibration curve has already been checked.[6] This allowed us to use the GPC curves to calculate the experimental $\overline{DP}_n$ of poly(CEVE)s. As may be seen in Table II, for all initiating systems including mixtures, a good agreement is observed between the experimental $\overline{DP}_n$ and theoretical ones calculated from the relationship

Table II
Polymerization of CEVE Initiated by a Mixture of HCl and HI Adduct, at −15 °C, in Toluene, in the Presence of Zinc Bromide ($[M]_0 = 1.6$ M, $[ZnBr_2] = 9 \times 10^{-3}$ M)

initiators, 10^{-3} M		$\bar{M}_n$(theor)			
R^aI	R^aCl	*b*	*c*	$\bar{M}_n$(exptl)	I
27	23	3400	6300	3300	1.13

[a] $CH_3CHOCH_2CH_2Cl$. [b] Assuming complete initiation by RI and RCl. [c] Assuming only initiation by RI.

Chart II



$$\overline{DP}_n = \frac{[CEVE]_0}{[RCl] + [RI]}$$

As shown in Figure 2, MWDs are monomodal and remain narrow (I is less than 1.2 for the mixtures) whatever the composition of the initiating system. These results suggest that each chain end is successively under the form of a chloride part of the time and the rest of the time is under the form of an iodide terminus. This condition is necessary for all macromolecules to grow at the same rate.

A similar situation also prevails in a less polar solvent such as toluene. As can be seen in Table II, initiation of the polymerization by mixtures of Cl and I adducts leads to poly(CEVE) also characterized by a monomodal and narrow ($I < 1.1$) MWD and $\bar{M}_n$ in agreement with chain initiation by both the chloro and iodo adducts.

It can be noticed that the same experimental approach was conducted in the case of iodine-activated systems. Although the chloro adduct–iodine combination was found active enough to initiate the polymerization of CEVE, experimental $\bar{M}_n$ were not in good agreement with the ones calculated by assuming a living mechanism. Therefore, this system was not appropriate to characterize the nature of active species in iodine-activated systems.

The results obtained with mixed initiating systems activated by zinc halides are fully consistent with a reaction pathway involving rapid exchanges (with respect to the polymerization rate) between terminal halides.

Two different mechanisms of halide exchange can again be considered: (1) a covalent one involving a 6-membered multicenter rearrangement, eventually with the participation of the incoming monomer (Chart II); (2) the ionization of carbon–halide ends assisted by the zinc salts, illustrated in Scheme II.

Both are consistent with the observed results with mixed initiating systems. Several experimental facts, however, tend to support an ionic mechanism:

(1) Polymerization rates are dependent on solvent polarity. The polymerization of CEVE in CH_2Cl_2 proceeds 3–5 times faster than in toluene.

(2) Reactivity of halide end groups increases with the decreasing dissociation energy of the carbon–halide bond.

$$\text{reactivity}^{1}\ \text{C–I} > \text{C–Br} \gg \text{C–Cl}$$

Further studies concerning the mechanism of the living polymerization of vinyl ethers are in progress.

Experimental Section. Materials. The chloro adduct of CEVE was synthesized by addition of HCl gas to CEVE in ethyl ether at 20 °C. After about a 2-h reaction time, the solvent and HCl in excess were distilled off and the adduct was stored in bulk under nitrogen at 0 °C.

Handling and purification of solvents, monomer, initiator, and catalyst have been described elsewhere.[6]

Polymerization Procedure. The polymerization of CEVE has already been described.[6] Mixed initiating systems were obtained in situ by introducing in a dilatometer, successively, the solvent, the chloro adduct, the monomer, and HI. Addition of the catalyst starts the polymerization process.

References and Notes

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Registry No. CEVE, 110-75-8; HCl, 7647-01-0; HI, 10034-85-2; $ZnCl_2$, 7646-85-7; Mn, 29160-08-5; ZnI_2, 10139-47-6; $ZnBr_2$, 7699-45-8.