Activated α-Chloro Ether and α-Bromo Ether End Groups as Propagating Species for the Living Cationic Polymerization of Vinyl Ethers

Since the pioneer work of Higashimura, in 1984,[1] in the field of living polymerization of vinyl ethers initiated by HI/I_2 systems, there has been much progress in the understanding of the key parameters that govern these polymerization reactions. It is now admitted that the covalent iodo polymer end groups can be temporarily activated (polarized or ionized) by electron acceptors.[2,3]

Various types of activators, including iodine, Lewis acids,[4,5] and ammonium salts,[5] have been used in order to assist the iodide end for monomer insertion. Besides, only α-iodo ether and very recently phosphate[6] termini have been described as the covalent ending being susceptible to activation. We have found that α-chloro ether and α-bromo ether functions can be activated for vinyl ether insertion by weak Lewis acids, in the same way as the corresponding iodide: the living character of the polymerization of vinyl ethers, chloroethyl vinyl ether (CEVE) being chosen as a model, is also preserved.

Polymerization of CEVE Initiated by 1,4-Bis(1-chloro-1-methylethyl)benzene (Cl-DiPB) or 1,4-Bis(1-bromo-1-methylethyl)benzene (Br-DiPB) and Zinc Iodide. Cl-DiPB and Br-DiPB have been prepared by direct addition, respectively, of an excess of dry HCl and HBr on DiPB, in hexane solution, Scheme I.

After about 2 h of reaction, residual HX and hexane were evacuated under vacuum and the addition products stored under N_2.

Quantitative formation of the dihalogeno adducts was confirmed by ^1H and ^{13}C NMR.

These two derivatives could not initiate per se the polymerization of CEVE, very likely because the carbon halogen bonds are not enough polarized or ionic in toluene or methylene dichloride. However, addition of a small amount of zinc iodide (>2%, molar, with respect to the halogeno precursor; see Table I) was sufficient to allow CEVE insertion into the carbon chloride and carbon bromide bonds of Cl-DiPB and Br-DiPB (Scheme IIa) as well as its subsequent incorporation into the resulting α-halogeno ether bond (Scheme IIb).

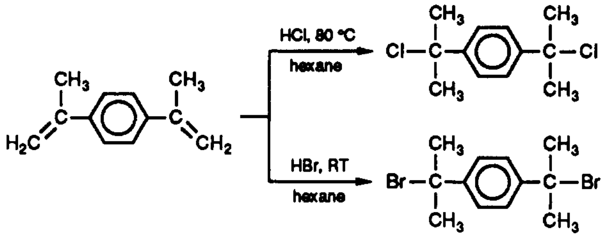
Figure 1 shows the course of the polymerization of CEVE at −30 °C along with Cl-DiPB/ZnI_2 and Br-DiPB/ZnI_2, under the same experimental conditions. The Br-DiPB/ZnI_2-initiated polymerization proceeded much faster than the corresponding chlorinated system, but both polymerizations went to completion.

The molecular weights $\bar{M}$ of the polymers increased linearly with a converted amount of monomer, and though based on a polystyrene calibration $\bar{M}_n$'s were in good agreement with the calculated values assuming that one DiPB contains two HX units but formed one polymer chain (Table I).

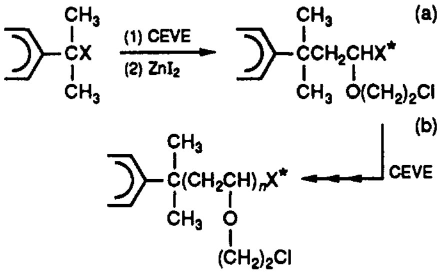
The proton NMR analysis of the polymers, Figure 2, reveals the presence of the methyl and aromatic groups of DiPB along with the peaks of the CEVE units. Relative intensities of DiPB peaks, given for one polymer in Table I, are in agreement with one DiPB unit incorporated per polymer chain.

The MWD of the polymers are quite narrow and in the range 1.2–1.3. This is, however, a little broader than generally observed with monofunctional HI/ZnI_2, possibly because of the bifunctionality of the initiators and/or of a relatively slow first CEVE insertion, as suggested by the presence in some kinetic curves of a slight induction period (Figures 1 and 3).

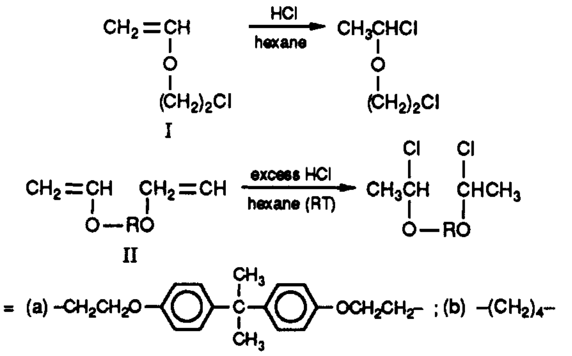
Scheme I



Scheme II



Scheme III[a]



Scheme IV

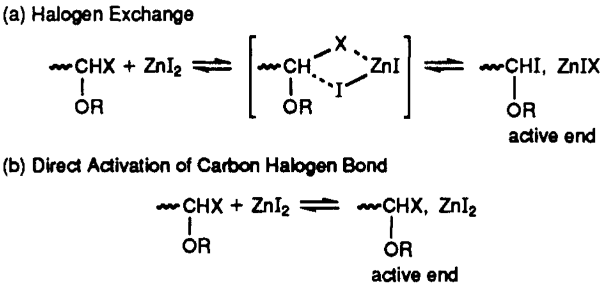


Table I
Polymerization of CEVE Initiated by Cl-DiPB/ZnI_2 and Br-DiPB/ZnI_2 Systems[a]

initiator	[initiator]/ [ZnI_2]	[CEVE]/ [initiator]	$\bar{M}_n$ theor	$\bar{M}_n$ exptl[b]	$\bar{M}_w/\bar{M}_n$	[CEVE unit]/ [aromatic]
Cl-DiPB	55	15.8	1880	1 900	1.3	14.5
	30	90.6	9840	10 800	1.3	
Br-DiPB	10	58	6370	7 300	1.3	
	30	90.6	9840	10 500	1.25	

[a] Solvent CH_2Cl_2, $T = -30$ °C, [CEVE] = 2.9 M. [b] From GPC, polystyrene calibration.

Polymerization of CEVE Initiated by α-Chloro Ethers and Zinc Iodide. In order to reduce the possible effect of the initiation step corresponding to CEVE insertion into the CX linkage of DiPB derivatives, their replacement by vinyl ether adducts was examined. The synthesis of α-chloro vinyl ether derivatives was achieved as already described for DiPB by reacting an excess of

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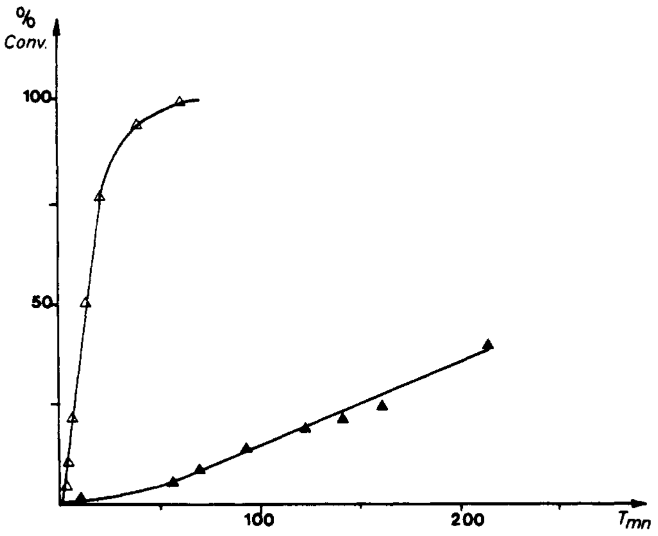

Figure 1. Time–conversion curves for the polymerization of CEVE initiated by Cl-DiPB/ZnI_2 (▲) and Br-DiPB/ZnI_2 (△) systems in CH_2Cl_2 at −30 °C: dilatometric study, [CEVE] = 2.9 M; [initiator] = 3.3×10^{-2} M; [initiator]/[ZnI_2] = 30.

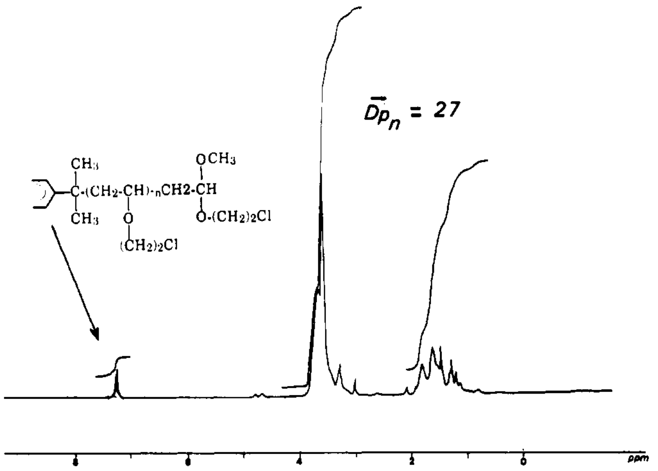

Figure 2. Proton NMR spectra of a polyCEVE obtained with a Cl-DiPB/ZnI_2 initiating system.

Table II
Polymerization of CEVE Initiated by α-Chloro Ethers and ZnI_2[a]

initiator	[CEVE]/[initiator]	$\bar{M}_n$ theor	$\bar{M}_n$ exptl[b]	$\bar{M}_w/\bar{M}_n$
I-HCl	9.1	1010	970	1.2
IIa-HCl	21.8	2750	2800	1.2
IIb-HCl	30	3630	3250	1.2
IIb-HCl	77	8400	8000	1.25

[a] Solvent CH_2Cl_2, −30 °C, [CCl]/[ZnX_2] = 15–30. [b] From GPC, polystyrene calibration.

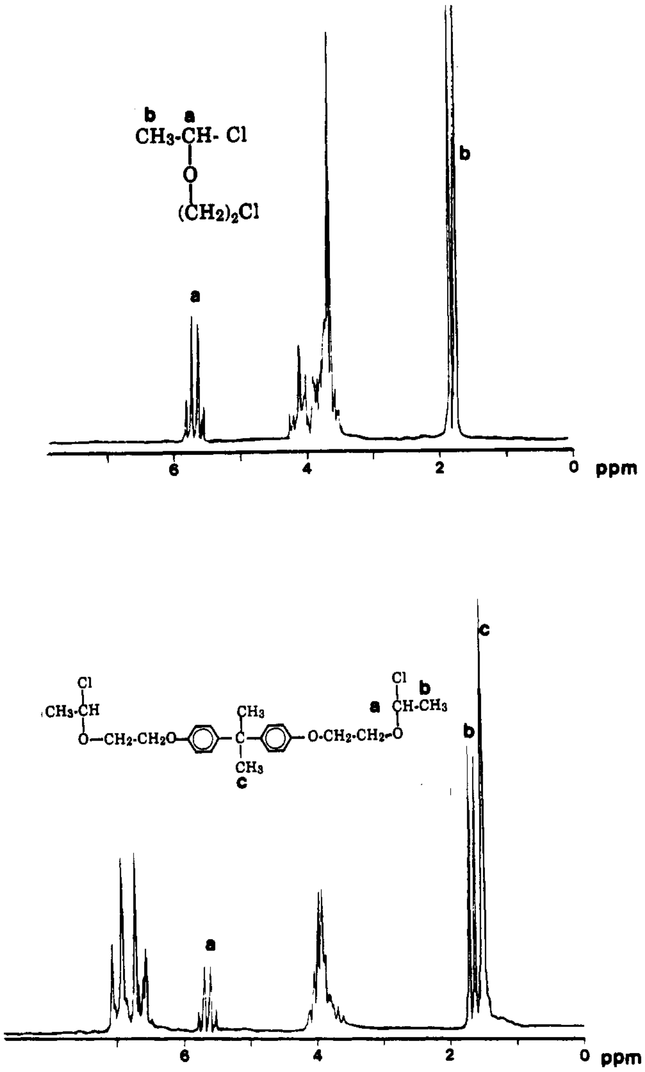

Figure 3. Proton NMR spectra of compounds I + HCl and II_a + HCl in $CDCl_3$.

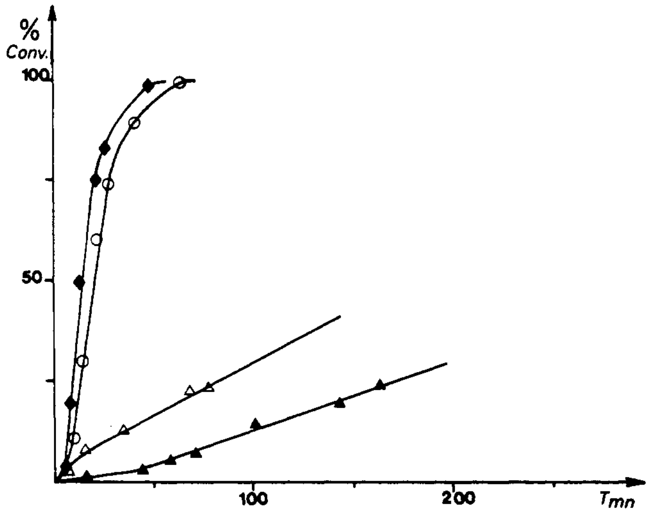

Figure 4. Kinetics of the polymerization of CEVE initiated by Cl-DiPB or Br-DiPB in the presence of ZnX_2: Cl-DiPB/ZnI_2 (▲); Cl-DiPB/$ZnCl_2$ (△); Br-DiPB/ZnI_2 (♦); Br-DiPB/$ZnBr_2$ (○) in CH_2Cl_2 at −30 °C; [CEVE] = 2.5 M; [CEVE]/[initiator] = 3.3 × 10^{-2} M; [initiator]/[ZnI_2] = 30.

HCl on vinyl ethers I and II, Scheme III.

Quantitative addition of HCl on vinyl ethers I and II was confirmed by ^{13}C and ^{1}H NMR (Figure 3).

Interestingly, these adducts are stable under N_2 at room temperature for days, allowing their preparation in advance.

Polymerizations of CEVE with chloro adducts of I and II along with ZnI_2 were performed in CH_2Cl_2, at −30 °C. Some typical data are collected in Table II. Results agree well with a living polymerization of CEVE, and MWD are slightly narrower than those observed with aromatic hydrocarbon initiators.

Nature of the Activated α-Halogeno Ether Termini Involved in Propagation. Since, in these polymerization systems, the initially formed chloride and bromide end groups were activated for CEVE insertion by zinc iodide, a possible halogen exchange, illustrated in Scheme IVa, could be operative: transient formation of a ZnXIactivated carbon–iodide terminal could then be considered instead of a direct activation of carbon–chloride or carbon–bromide terminals by ZnI_2, Scheme IVb.

In order to differentiate between these two hypotheses, the polymerization of CEVE, intiated with Cl-DiPB along with zinc chloride and zinc iodide and with Br-DiPB along with zinc bromide and zinc iodide as activators,[7] was investigated. Results presented on Figure 4 show that the polymerization activity is at least maintained in systems free of iodide, which is consistent with a direct activation of α-chloro ether and α-bromo ether ends by zinc halide, as already proposed for iodide ends.[2]

This shows that living cationic polymerization of vinyl ethers can be achieved from relatively covalent end groups such as chloride or bromide termini along with an appropriate Lewis acid activator. An important advantage of the carbon–chloride end group with respect to the halide is its good stability under nitrogen up to room temperature. This allows, for example, the preparation and characterization of well-defined multifunctional initiators and their storage prior to the polymerization. A more detailed investigation of these systems is in progress.

References and Notes

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CORRECTIONS

Werner Mormann* and Martin Brahm: Polymers from Multifunctional Isocyanates. 5. Synthesis of Liquid-Crystalline Polyurethanes from Methyl-Substituted Diisocyanato-Substituted Benzoates. Volume 24, Number 5, March 4, 1991, p 1098.

The correct Figure 1 and its caption are as follows:

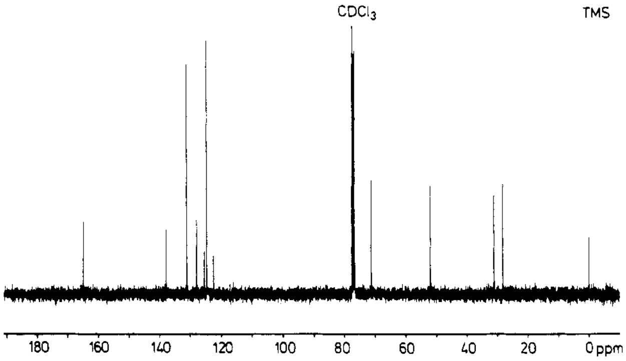

Figure 1. ^{13}C NMR spectrum of *trans*-4-isocyanatocyclohexyl 4-isocyanatobenzoate (12).