

## **Kinetic study of the polymerization of chloro ethyl vinyl ether initiated by the system hydrogen iodide / iodine**

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### Summary

A kinetic study of the cationic polymerization of chloroethyl vinyl ether initiated by the system hydrogen iodide - iodine has been performed in order to understand some particular characteristics of the system. As previously reported by Higashimura the polymerization shows a living character at low temperature in toluene. A polymerization process with a first order in iodine and 0.3 order with respect to monomer, has been observed. These results are consistent with the existence of reversible elementary processes involving iodine and monomer.

### Introduction

In the last years, relevant progress have been accomplished in the field of cationic polymerization of vinyl monomers. Several couples monomer-initiating systems leading to polymerizations with a "living" character, have been reported allowing the synthesis of new functional polymers. The main contributions to this breakthrough have been those of Kennedy et al. (isobutylene-inifer systems) and of Higashimura et al. (vinyl ethers polymerization by hydrogen iodide associated to iodine). Vinyl ethers represent a class of monomers which can lead, according to the variety of the substituents linked to the vinyl ether function, to broad class of materials (1-4). Interestingly, even in the case of functional side groups, the living nature of the polymerization process may be preserved. The polymerization of chloroethyl vinyl ether initiated by hydrogen iodide / iodine, recently investigated by Higashimura (3) may be cited as one of these exemples. Despite some destabilizing effect of the chlorine atom the polymerization shows a living character, at low temperature in non polar solvent.

We have been recently involved in the synthesis of mono and bifunctional polyvinyl ethers with reactive lateral side groups in order to prepare new block copolymers and networks. In the course of these synthesis our attention has been focused on some of the characteristics of the "living" polymerization of chloroethyl vinyl ether (CEVE) not satisfactorily explained by the mechanism proposed by Higashimura (5).

In order to better understand the polymerization process, kinetic studies of the polymerization of CEVE, initiated by hydrogen iodide-iodine have been conducted in toluene at - 27°C.

### Experimental

Materials : Chloroethyl vinyl ether (Aldrich) was purified by distillation over calcium hydride and stored under nitrogen in a flask

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equipped with PTFE stopcocks over calcium hydride. Toluene and n-hexane (S.D.S.) were distilled over calcium hydride and stored in a flask containing a small amount of polystyryllithium. CEVE, toluene and n-hexane were distilled under vacuum just before use. Iodine was sublimed and stored in the dark, under nitrogen, in toluene or n-hexane solution. Hydrogen iodide was obtained from a 57% aqueous solution (Aldrich) by dehydration in toluene or n-hexane with phosphorus pentoxide (6). The organic solution was twice cryodistilled under vacuum and stored under dry  $N_2$  at  $-30^\circ C$ . Titration of the HI solution was made in aqueous solution with a 0.1 N sodium hydroxide solution by pH-metry.

#### Procedures :

Polymerizations of CEVE were performed under vacuum, at controlled temperature, in a glass reactor equipped with PTFE stopcocks and septa. Solvent and monomer were first introduced with syringues. The solution was frozen in liquid nitrogen, evacuated, and the suitable amount of an HI solution was then introduced by cryodistillation in the reactor. Temperature of the solution was then slowly raised up to the polymerization temperature. Polymerization was started by injection of the iodine solution.

Monomer conversion was followed by sampling the reaction mixture in a side tube isolated by a stopcock and in which deactivation was immediately performed, at low temperature, by adding ammoniacal methanol. Conversions were determined by gas chromatography with chlorobenzene as internal standard. MW were determined for each sample directly by G.P.C. analysis of the crude deactivated solutions.

At final conversion, the reaction medium was deactivated as before, washed as indicated in (4) and the polymer solution recovered by decantation. Polymers were obtained by evaporation of the solvent under vacuum.

G.P.C. measurements were performed on a Varian Vista 5500 chromatograph fitted with 4 TSK gel columns calibrated with polystyrene standards.

#### Results and discussion

In a first time, we examined the variation of the monomer conversion versus time. Figure 1 shows a linear relationship conversion-time up to 100% conversion. Addition of a new monomer feed,  $M'_0$ , to the completely polymerized solution, resulted in another complete monomer consumption. The new polymerization proceeds at the same rate and, surprisingly according to the same linear conversion time relationship, suggesting a kinetic law with an apparent zero order with respect to monomer. Similar behaviour was recently observed by Cho et al. for n-butyl vinyl ether polymerization (7).

Polydispersities of the polymers formed are in the range 1.1 to 1.3. In figure 2, experimental  $\bar{M}_n$ , determined by G.P.C., are plotted versus the amount of monomer polymerized.

Number average molecular weights are directly proportional to the amount of CEVE consumed, up to the end of reaction thus corroborating the apparent living character of the polymerization. Experimental  $\bar{M}_n$  values are however lower than those calculated by the equation :

$$\bar{M}_{nth} = M_{CEVE} \cdot [\text{Polymer}] / [\text{HI}]_0$$

$$\bar{M}_{nexp} / \bar{M}_{nth} \sim 0.7$$

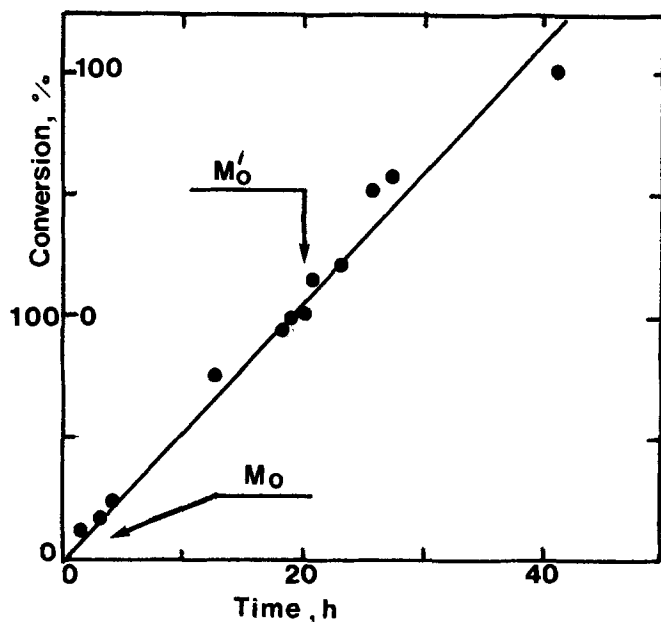


Fig. 1 : Typical time-conversion plots for the polymerization of CEVE in toluene at  $-27^{\circ}\text{C}$ .  $[\text{M}]_0 = 0.42 \text{ M}$   
 $[\text{M}'_0] = 0.55 \text{ M}$   
 $[\text{HI}]_0 = 17 \text{ mM}$   
 $[\text{I}_2]_0 = 3.2 \text{ mM}$

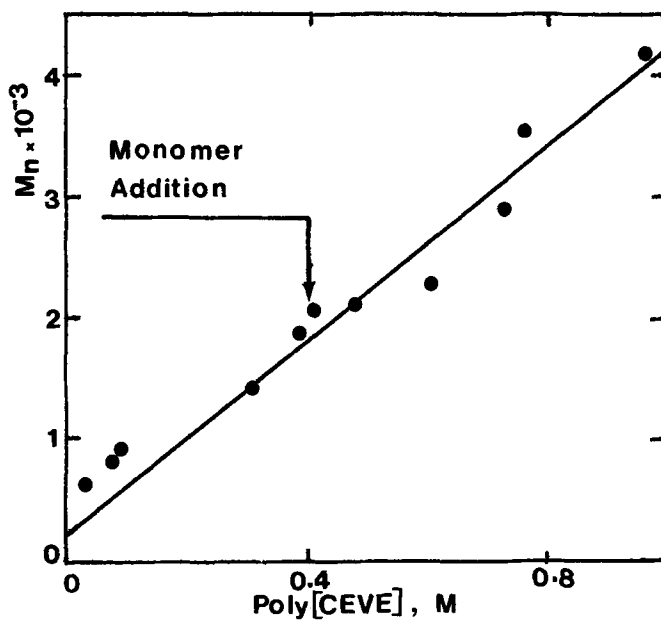


Fig. 2 : Variation of  $M_n$  with the amount of poly(CEVE) in toluene at  $-27^{\circ}\text{C}$   
 $[\text{M}]_0 = 0.42 \text{ M}$   
 $[\text{M}'_0] = 0.56 \text{ M}$   
 $[\text{HI}]_0 = 17 \text{ mM}$   
 $[\text{I}_2]_0 = 3.2 \text{ mM}$

The discrepancy between experimental and theoretical  $\bar{M}_n$  might be due to the nature of the calibration standards used for G.P.C. measurements. To clarify this point, determinations of  $\bar{M}_n$  by VPO and by end-groups titration are in progress.

In order to confirm the effects of monomer concentration on the rate of polymerization, experiments were performed with different initial monomer concentrations ranging from 0.1 to 2 M. The log-log plots of  $R_p$  versus  $[M]_0$  are given in figure 3. Within the experimental error, a linear relationship is observed with a slope which leads to an apparent 0.3 monomer order.

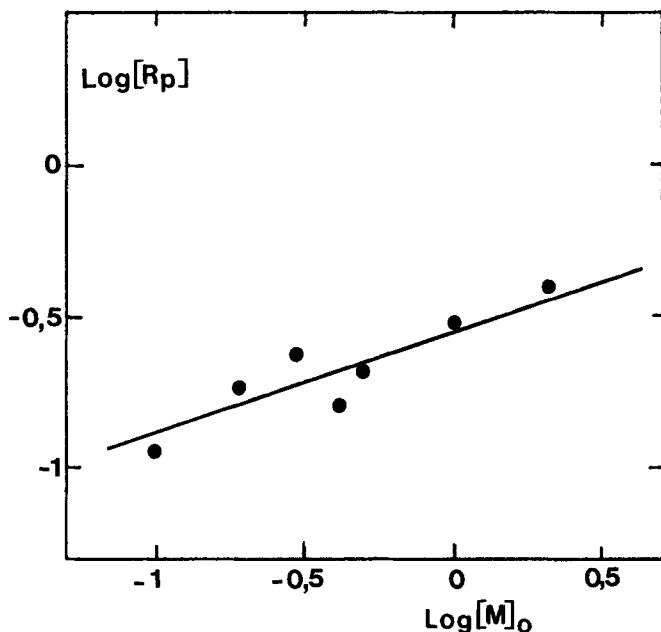


Fig. 3 : Determination of the monomer order

$$[M]_0 = 0.1 - 2 \text{ M}$$

$$[HI]_0 = [I_2]_0 = 17 \text{ mM}$$

Effect of hydrogen iodide and of the concentration in iodine on the polymerization rate, have also been examined. HI alone adds rapidly and quantitatively to CEVE even in stoichiometric conditions but no further monomer insertion into  $\alpha$ -iodoether bonds was observed in absence of iodine.

The polymerization rate dependence in iodine concentration for fixed monomer and hydrogen iodide concentrations is presented on figure 4.  $R_p$  increases linearly with increasing  $I_2/IH$  ratio in the range 0 to 1.5.

The contribution of iodine to a secondary polymerization process involving direct initiation by iodine, has also been considered. Kinetics of polymerizations directly initiated by iodine are compared to those of the corresponding  $I_2/HI$  systems. Results represented in fig. 5 show that the  $I_2$  initiated polymerization may be neglected compared to the  $I_2/HI$  initiated process. This is also confirmed by the absence of significant variation of  $\bar{M}_n$  when  $I_2$  is markedly increased. The corresponding results are given in table 1.

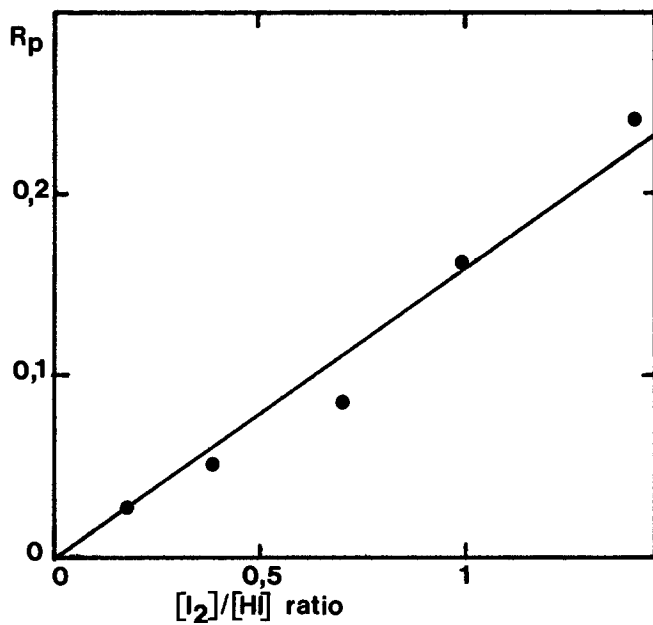


Fig. 4 : Dependence of  $R_p$  on the  $I_2/HI$  ratio,  $[HI]_0 = 17 \text{ mM}$ ,  $[M]_0 = 0.42 \text{ M}^0$

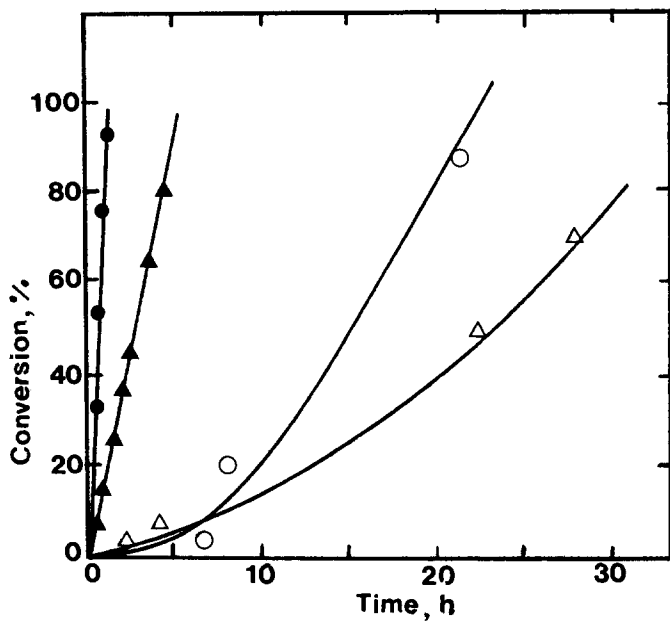


Fig. 5 : Comparative study of the polymerization of CEVE initiated by  $I_2/HI$ , or  $I_2$ , in toluene at  $-27^\circ\text{C}$ .

$[HI]_0 = [I_2]_0 = 17 \text{ mM}$   
 $[M]_0 = 0.2 \text{ M}$  ●  
 $[M]_0 = 2 \text{ M}$  ▲

$[I_2]_0 = 17 \text{ mM}$   
 $[M]_0 = 0.2 \text{ M}$  ○  
 $[M]_0 = 2 \text{ M}$  △

Table 1 : Effect of the Iodine concentration on the  $\bar{M}_n$  of poly CEVE obtained at  $-27^\circ\text{C}$  in toluene,  $[\text{M}]_0 = 0.42 \text{ M}$   $[\text{IH}] = 17 \text{ mM}$

$[\text{I}_2] \text{ mM}$	$\bar{M}_n$ (at 100% conversion)
3.2	1920
6.5	2300
12	2020
17	2570
24	2225

The log-log plot of  $R_p$  versus  $\text{I}_2$  concentration is shown on figure 6. Data are in agreement with a first-order in iodine.

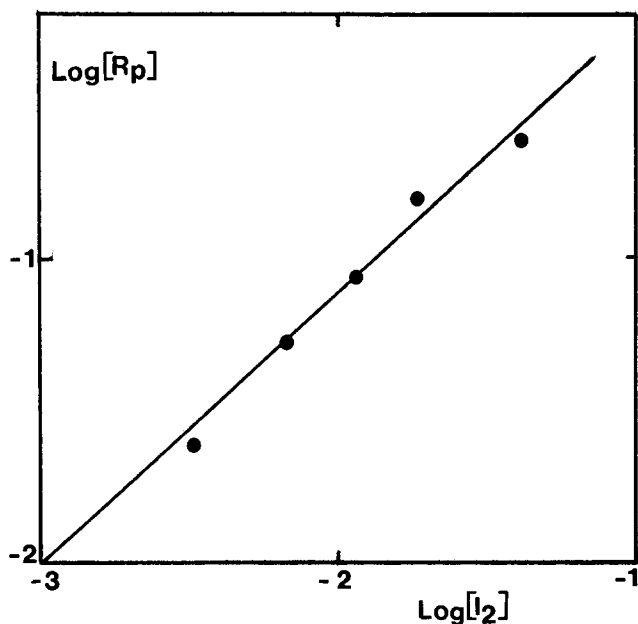
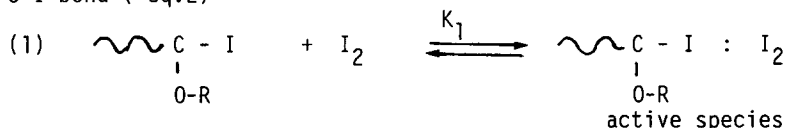


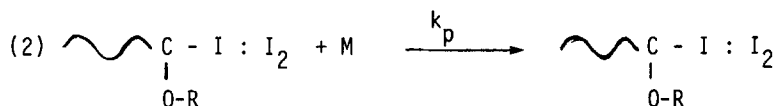
Fig. 6 : Determination of the order on iodine  $[\text{M}] = 0.42 \text{ M}$ ,  $[\text{HI}]_0 = 17 \text{ mM}$

For the CEVE polymerization, the whole of the results can be summarized by the following kinetic equation :

$$R_p = k_p [\text{HI}] [\text{I}_2] [\text{M}]_0^{0.3}$$

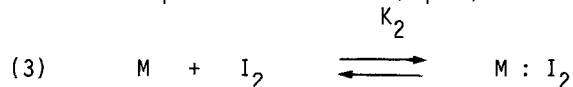
According to Higashimura (5) the propagation mechanism would involve an activation of carbon-iodide polymer ends by iodine (equation 1). Propagation would proceed via the insertion of monomer into the activated C-I bond (eq.2)



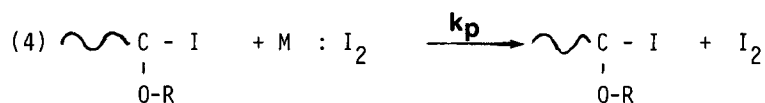


A kinetic scheme involving equations 1 and 2 only leads to a first order dependence of the polymerization both in iodine and in monomer. This is not in agreement with our experimental findings.

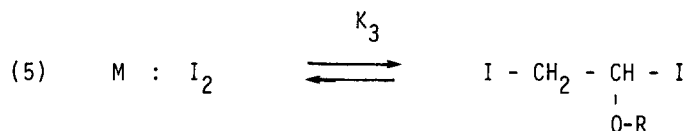
Recently Cho et al. (6) suggested that iodine might also form a charge transfer complex with monomer (eq. 3)



which might activate monomer and allow its insertion into the polymer alkyl iodide bonds,



However, other authors (8,9) consider that the monomer-iodine complex is unstable and rapidly gives the diiodo adduct through a reversible addition process.



Taking into account in the polymerization mechanism either the monomer charge transfer complex or the reversible adduct formation one can write a kinetic expression with a complex monomer dependence varying from zero to first-order, according to the value of constants of the various equilibrium involving the monomer molecule. Experimental data strongly suggest that reversible monomer-iodide interactions play an active role in the CEVE polymerization. The nature and the extent of these reversible elementary reactions are presently under investigation.

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