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Polymerization of 2-phenyl-aziridine

A kinetic study

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SUMMARY

The ring-opening polymerization of 2-phenyl aziridine was studied with several catalyst systems : boron trifluoride etherate, chlorhydric acid, perchloric acid, dimethyl sulfate and methyl triflate. The corresponding polyamine was obtained as a pale yellow solid with a number average molecular weight around 2,000 – 3,000.

A kinetic study is discussed in the case of perchloric acid and methyl triflate.

INTRODUCTION

It is well known that the cationic ring opening polymerization of aziridines is not very suitable for the synthesis of high molecular weights polyamines because of the importance of chain transferand termination reactions[1,5]. There are however some few exceptions such as for examples 1 – tert.butyl aziridine and 1-benzyl aziridine[6]. In these cases, the presence of a bulky substituent on the nitrogen decreases the termination and transfer reactions but also reduces the rate of the propagation step. The introduction of one or two substituents on a carbon of the aziridine ring dramatically decreases the reactivity of the monomer ; generally 1-2 disubstituted aziridines do not polymerize[7].

There are rather few examples in the literature of the behaviour of 2-substituted aziridines and it seemed to us of interest to attempt the ring opening polymerization of 2-phenyl aziridine.

RESULTS AND DISCUSSION

The reaction can be initiated with several catalysts such as boron trifluoride etherate, chlorhydric acid, perchloric acid, methyl trifluoromethane

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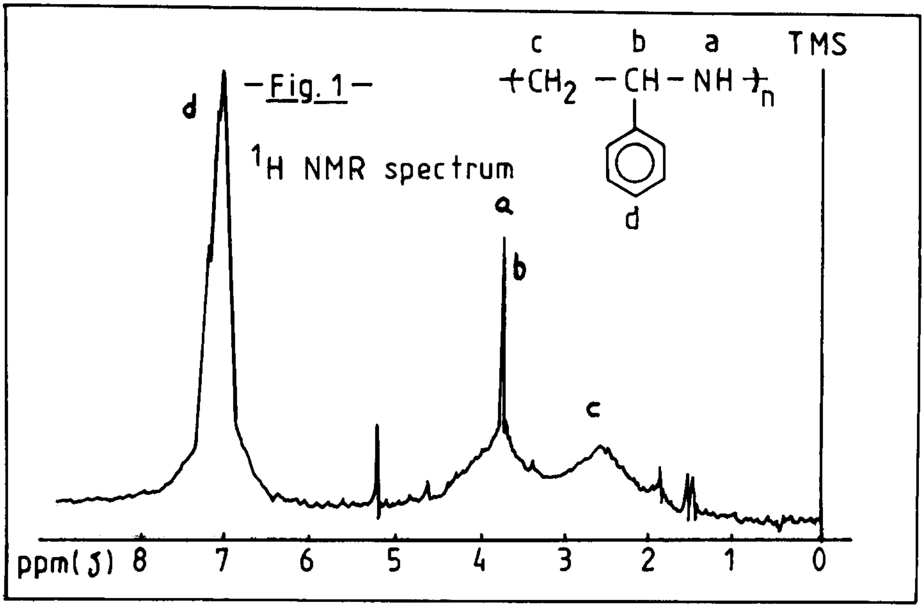
sulfonate and dimethyl sulfate. In spite of the aformentionned drawbacks a polymer with a number average molecular weight around 2,000-3,000 was obtained. The isolated product is a yellow solid insoluble in ether and water, soluble in methylene chloride, chloroform and tetrahydrofuran. Molecular weights were determined on GPC column using the polystyrene calibration and by vapor pressure osmometry. The ^{1}H NMR spectrum of the polymer is shown in figure 1.

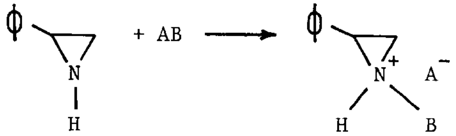

-Fig. 1-

^{1}H NMR spectrum

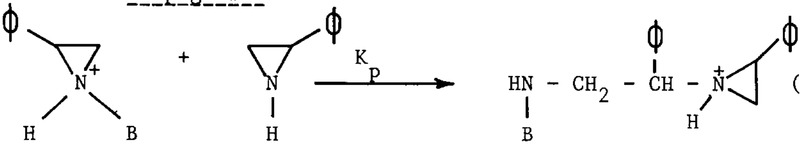
Kinetics and Mechanism

The mechanism of the polymerization can be described as follows :

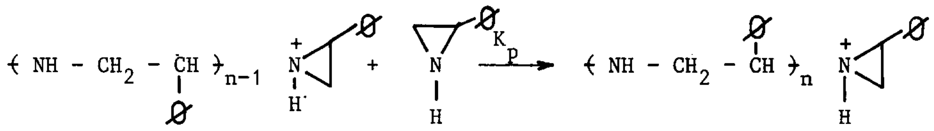
Initiation



Propagation

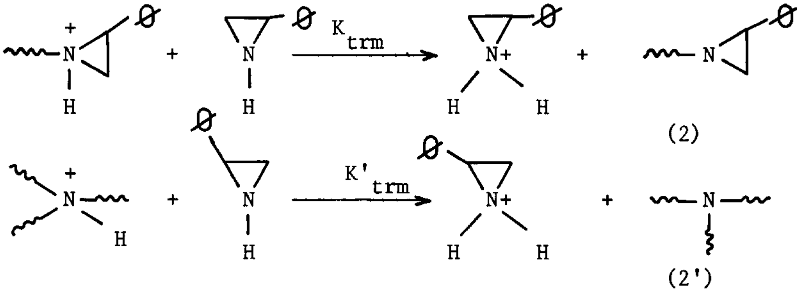


(1)



Termination and Transfer

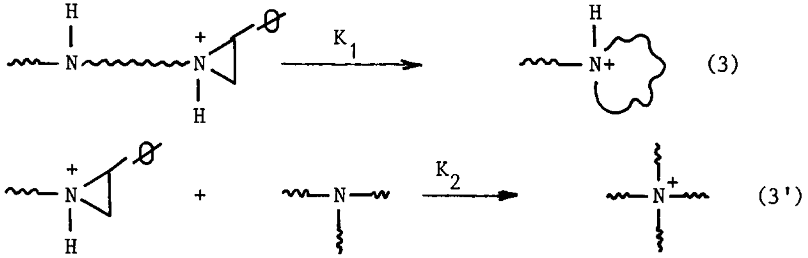
Transfer to the monomer :



(2)

(2')

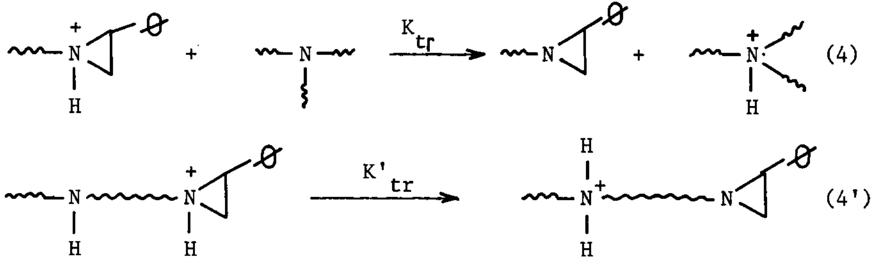
Ring opening through a nitrogen along the chain :



(3)

(3')

Transfer to a nitrogen along the chain :



(4)

(4')

The following abbreviations are used in our equations :

M : monomer concentration with M_o : initial concentration

M_f : final concentration

M_n^+ : active species concentration

C_o : initial concentration of the initiator = M_{no}^+

N^+ : concentration in chains bearing protons arising from trnasfer reactions (not including the aziridine cycle) $N^+ = C_o - M_n^+$

N : concentration in species different from the monomer : $(M_o - M)$.

Hypothesis and approximations

In order to establish the equations relative to the above mentioned reactions, we need to bring forward some simplifications. For that purpose, we assume at first that the termination reaction is the deactivation through the opening of the otrained ring[5]. We neglect then the nucleophilic action of the counterion A^-, which is supposed to be sufficiently stable. This supposes also that the transfer reaction which consists of activating the aziridine ring through an ammonium salt $>\overset{+}{N}<$ is unlikely since the formation of $>\overset{+}{N}<$ is considered as a termination reaction. However, we cannot neglect the transfer from the active species to the monomer especially since the concentration of the later is large at the very beginning of the reaction. The second approximation consists in considering, from a formalistic point of view, that reactions (3) and (3') are identical as well as reactions (4) and (4'). The rate of monomer consumption is given by the sum of the rates of its consumption by reactions (1) and (2). :

$$\frac{-\,dM}{dt} = K_p M M_n^+ \quad + \quad K_{trm} M M_n^+ = (K_p + K_{trm}) \; M M_n^+ = K M M_n^+ \qquad (5)$$

$$\frac{-\,dM_n^+}{dt} = M_n^+ \; (M_o - M) \; (K_2 + K_{tr}) = K_t M_n^+ \; (M_o - M) \qquad (6)$$

with $K = K_p + K_{trm}$ and $K_t = K_2 + K_{tr}$

The curves giving the percentage of conversion as a function of time are depicted in figure 2. They show two stages : a first one with a high consumption of monomer, covering the major part of the conversion (until 80 to 90 %) and a second one with a rapid slow down until 98 % in a few cases. It is obviously in the second stage that the transfer to the monomer after exhaustion of the active specie allows a slow consumption of the monomer being left. Therefore, in order to remain in the frame of our model, we have to consider only the first stage.

Combining equations (5) and (6), we obtain :

$$\frac{dM}{dM_n^+} = \frac{K}{K_t} \frac{M}{(M_o - M)}$$

The integration leads to :

$$\log \frac{M_o}{M_f} - \frac{(M_o - M_f)}{M_o} = \frac{K}{K_t} \frac{C_o}{M_o} \qquad (7)$$

Degree of polymerization

In order to estimate it, we have to take into account the transfer to the monomer. If n is the numer of chains initiated through this transfer :

$$\overline{DP}_n = \frac{M_o - M_f}{C_o + n} \qquad \frac{dn}{dt} = K_{trm} M_n^+ M$$

$$\text{with} \quad \frac{-dM}{dt} = KM M_n^+$$

$$- \frac{dn}{dM} = \frac{K_{trm}}{K} \quad nf = n_{total} = \frac{K_{trm}}{K} (M_o - M_f)$$

$$\frac{1}{DP_n} = \frac{C_o}{M_o - M_f} + \frac{K_{trm}}{K}$$

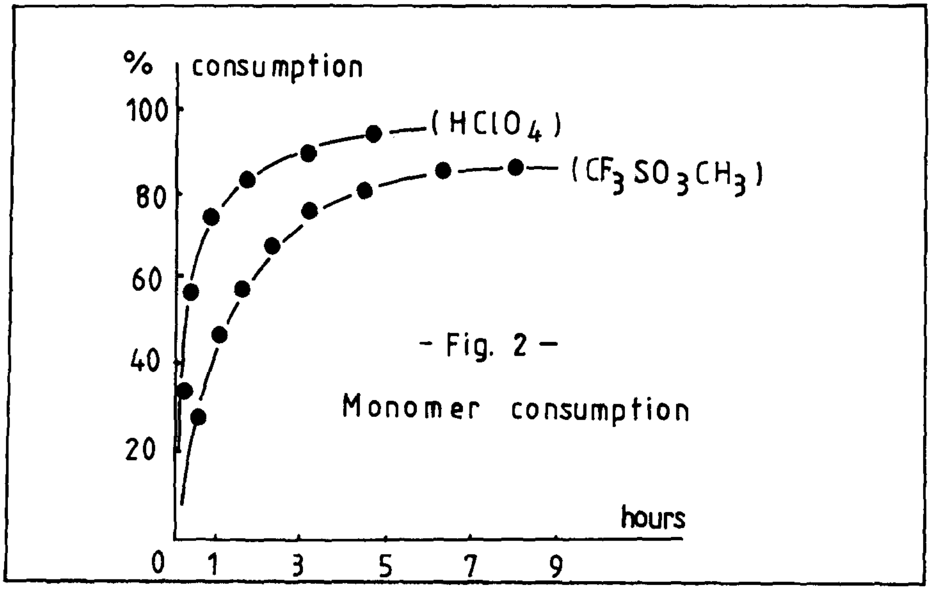
By varying the initial concentrations M_o and C_o and determining M_f from the conversion curve, one can then estimate $\frac{K}{K_t}$ for each experiment. (Table I).

Estimation of K

According to equation (5) $-\frac{dM}{dt} = K M M_n^+$, it is possible to estimate K from the slope at the origin ($t \longrightarrow 0$) of the curve M(t). In this case $M_n^+ \longrightarrow C_o$ and $M \longrightarrow M_o$.
This slope is therefore equal to $KM_oC_o = P_o$
We find (fig. 2) :

$K = 35 \pm 5 h^{-1} l.mole^{-1}$ for $CF_3SO_3CH_3$

$K = 64 \pm 7 h^{-1} l.mole^{-1}$ for $HClO_4$



- Fig. 2 -

Monomer consumption

TABLE I : Determination of K/K_t

Initiator	M_o	C_o	M_f	K/K_t
	in mole/l			
$CF_3SO_3CH_3$	0.70	0.0170	0.1 M_o	58
"	0.53	0.0140	0.08 M_o	60
$HClO_4$	0.53	0.0174	0.1 M_o	42
"	0.53	0.030	0.05 M_o	36

Estimation of K_{trm}

The experimental determination of the final $\overline{DP}_n$ with standards of polystyrene, allows to reach K_{trm}/K (Table II).

It appears thus that the ratio K_{trm}/K is approximatively the same for the two initiators although the constants K are different, and that $\overline{DP}_n$ reachs a limit : if $K_{trm}/K = 0,035$ $(\overline{DP}_n)_{max} = 39$.

Indeed, the GPC spectra show a stteling toward the high molecular weights (2,500 - 3,000). We never achieved to even with other initiators, to prepare higher molecular weights wth this aziridine.

TABLE II : Determination of K_{trm}/K

Initiator	M_o	C_o	M_f	$\overline{DP}_n$(exp)	K_{trm}/K
	in mole/l				
$CF_3SO_3CH_3$	0.70	0.017	0.10 M_o	16.5	0.034
"	0.53	0.014	0.08 M_o	16	0.035
$HClO_4$	0.53	0.0174	0.1 M_o	13	0.040
"	0.53	0.030	0.05 M_o	11	0.031

CONCLUSION

The estimation of K_{trm} allows to determine K_p from K and to show that the opening of the cycle is far much probable than a simple transfer to the monomer $K_p >> K_{trm}$ (Table III).
We can assum the same behavior for reactions (3,3') and (4,4') and write $K_2 >> K_{tr}$.

TABLE III : Determination of the absolute constants (in $h^{-1}l.mole^{-1}$)

Initiator	K	K_t	K_p	k_{trm}
$CF_3SO_3CH_3$	35	0.58	33.5	1.4
$HClO_4$	64	1.6	61.4	2.6

The ratio K_p/k_t is higher with the initiator $CF_3SO_3CH_3$ than with perchloric acid. THis result clearly indicates that methyl triflate favours the polymerization by stabilizing better the aziridinium ion.

EXPERIMENTAL PART

Materials and methods

2-phenyl aziridine is obtained by hydrogenation with $LiAlH_4$ of the corresponding 2H aziridine[8].

$HClO_4$ was purchased from Merck and used without further purification.
The polymerization was carried out in a round bottom flask, under nitrogen to the monomer (0,5 to 1 g) in 5 to 10 ml of CH_2Cl_2 is added the initiator and the reaction miwture is refluxed during several hours. Removal of the solvent under reduced pressure affords the polyamine as a yellow solid.

Apparatus and measurements

Molecular weight approximations were accomplished by gel permeation chromatography (Waters Associates ALC 244). 100 and 500 Å µ styragel columns were used with a tetrahydrofuran solvent flow rate of 1 ml/min. Approximate calibration of the columns was accomplished by means of narrow molecular weight distribution standards obtained from Water Associates. N.M.R. spectra were obtained with a VARIAN EM 390 Spectrometer.

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