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# New synthesis of linear polyethyleneimine

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## SUMMARY

Linear polyethyleneimine was synthesized by the cationic ring-opening polymerization of N(2-tetrahydropyranyl)aziridine, followed by acidic hydrolysis of the corresponding substituted polyamine. The linear structure of the end product was proved by $^{13}$C-NMR spectroscopy and by its physical properties. Molecular weights up to 25,000 were obtained.

## INTRODUCTION

Commercial polyethyleneimine (PEI) which is obtained by cationic ring-opening polymerization of ethyleneimine, has a highly branched structure containing primary, secundary and tertiary amino functions (1). This high degree of branching is the result of the easy proton transfer from the tertiary aziridinium ion, which is the active species in the polymerization, to other amino functions present in the reaction mixture.
Up to now, the synthesis of linear polyethyleneimine (LPEI), containing secundary amino functions only, has been achieved by two methods :

1) cationic isomerization ring-opening polymerization of 2-oxazolines, followed by hydrolysis of the resulting polyamide (2)(3)
2) polycondensation reaction of N(2-aminoethyl)aziridine in aqueous medium (4)

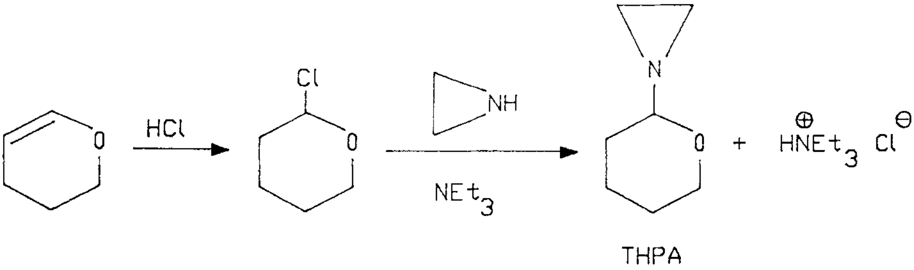
In the cationic ring-opening polymerization of N-alkylaziridines, the active species are quaternary aziridinium ions. Since transfer of an alkyl group does not occur, the corresponding polymers are in principle linear. With most N-alkylaziridines however, the formation of high molecular weight polymers is prevented by a termination reaction, which occurs when the active species reacts with a polymer amino function instead of monomer. It was found that introduction of a bulky substituent on the aziridine nitrogen decreases the termination rate constant considerably more than the propagation rate constant. The polymerization of N-tert.butylaziridine for example, has a high living character (5).

Considering these facts, new methods for the synthesis of LPEI were explored by polymerization of N-substituted aziridines in which the substituent had to meet four requirements : be bulky, be easily replaced by a hydrogen atom, not decrease the nucleophilicity of the amino function and not interfere with the cationic polymerization.
The present communication describes the first successful result obtained with N(2-tetrahydropyranyl)aziridine (THPA) as a monomer.

## RESULTS AND DISCUSSION

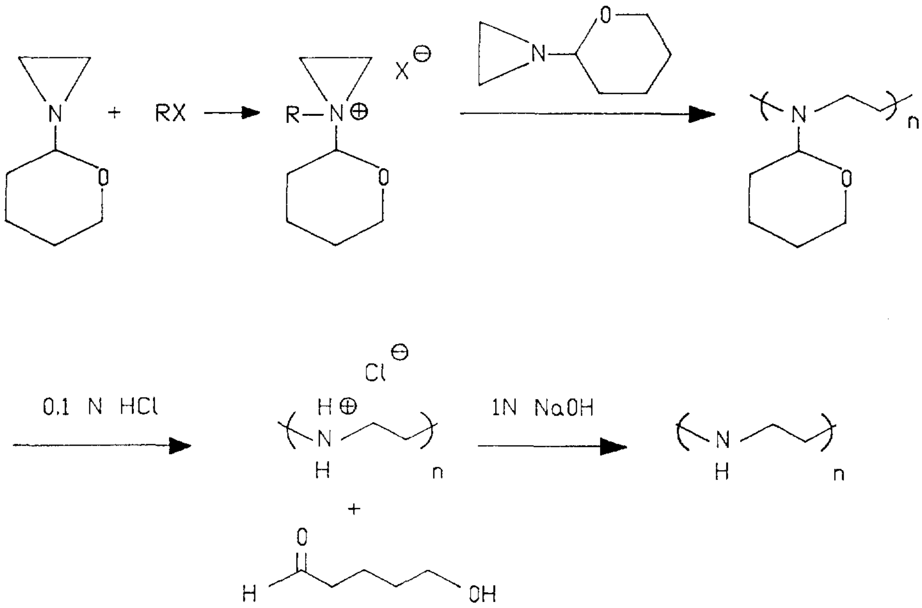
### Monomer

The synthesis of THPA has been described by Ricart et al.(6). This colorless liquid is formed by the reaction of ethyleneimine with 2-chlorotetrahydropyran which in turn is obtained by addition of hydrogen chloride to dihydropyran.
Using a slight modification of the preparation method given by Ricart, the overall-yield was 65%.



### Polymerization of THPA and hydrolysis to LPEI.

Low temperature bulk polymerization of THPA with typical cationic initiators leads to the formation of a transparent glassy material in high yield. The $^1$H-NMR spectrum of this polymer is in accordance with the structure of poly-THPA.
Hydrolysis of poly-THPA is achieved by dissolving it in 0.1 N aqueous hydrogen chloride at room temperature. Addition of sodium hydroxide results in precipitation of a white solid which was found to be pure LPEI.
Polymerization of THPA in acetonitrile at 0°C leads to incomplete conversion. The final yields depend on the initiator concentration. Apparently, a termination reaction, the nature of which is still obscure, is taking place here.



with RX = $CF_3SO_3CH_3$ , $BF_3.OEt_2$ , $Et_3OBF_4$

Characterization of the end product

The PEI obtained was analyzed by NMR, DSC and LALLS. The fact that the polymer is insoluble in cold water is a first indication that it is LPEI.
Figure 1 shows the $^{13}$C-NMR spectrum of the reaction product. For comparison the $^{13}$C-NMR spectrum of a commercial PEI is also shown (figure 2). The single peak at 49.5 ppm is in accordance with the value reported earlier by Tanaka (3) and Bartulin (7) and shows that it is very pure LPEI.
The glass transition temperature and melting point of the anhydrous LPEI were determined by DSC. A Tg of 245 K and a Tm varying between 313 and 320 K were obtained. These values are in agreement with the values reported by other autors (2)(3). In figure 3, the first DSC-run (A) shows the Tm of anhydrous LPEI and the melting region of the crystalline hydrate forms of LPEI which do not appear in the second run (B) of the same sample.
Table 1 shows polymerization yields and weight average molecular weights of LPEI's obtained by polymerization in bulk and in acetonitrile for different reaction conditions.

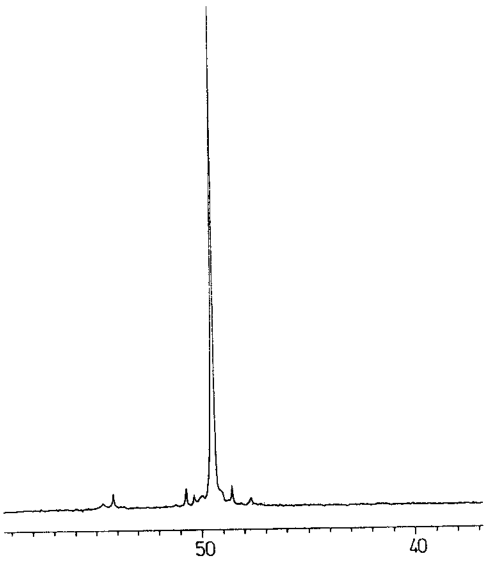


Fig. 1 : $^{13}$C-NMR spectrum of linear PEI (in $CDCl_3$)

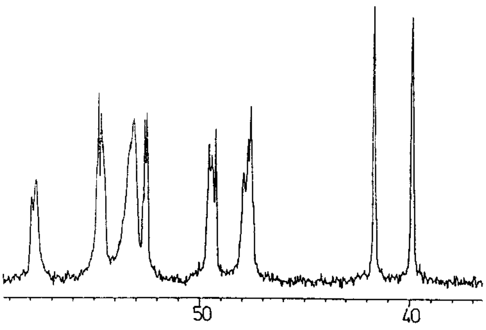


Fig. 2 : $^{13}$C-NMR spectrum of branched PEI (in $D_2O$).

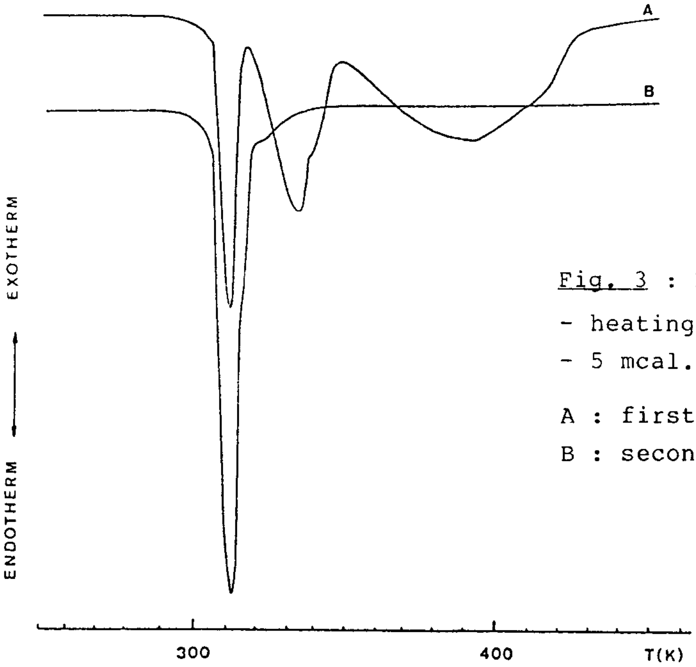


Fig. 3 : DSC-curves of LPEI

- heating rate: 20°C.min$^{-1}$
- 5 mcal.s$^{-1}$.

A : first run

B : second run

Table 1 : Polymerization of THPA in bulk and in acetonitrile : weight average molecular weights and polymerization yields

Bulk$^{a)}$

| Initiator | [In]/($10^{-5}$ mole) | $M_{w,LPEI}$$^{c)}$ | Yield (%) |
|---|---|---|---|
| $CF_3SO_3CH_3$ | 1.94 | 19600 | >90 |
| $CF_3SO_3CH_3$ | 2.65 | 16300 | >90 |
| $BF_3.OEt_2$ | 4.42 | 16500 | >90 |
| $Et_3OBF_4$ | 2.65 | 15200 | >90 |
| $Et_3OBF_4$ | 4.42 | 13600 | >90 |

$CH_3CN$$^{b)}$

| Initiator | [In]/($10^{-2}$ mole.$l^{-1}$) | $M_{w,LPEI}$$^{c)}$ | Yield (%) |
|---|---|---|---|
| $CF_3SO_3CH_3$ | 0.66 | 18200 | 47 |
| $CF_3SO_3CH_3$ | 1.10 | 10600 | 50 |
| $CF_3SO_3CH_3$ | 1.76 | 13500 | 55 |
| $Et_3OBF_4$ | 0.66 | 7300 | 45 |
| $Et_3OBF_4$ | 1.10 | 11200 | 48 |
| $Et_3OBF_4$ | 1.76 | 9000 | 54 |

a) $7.8 \times 10^{-3}$ mole THPA
T = -65°C $\longrightarrow$ -25°C
Reaction time = 30 min

b) $c_{THPA} = 1.95$ mole.$l^{-1}$
T = 0°C
Reaction time = 60 min

c) Determined by LALLS in MeOH at 25°C

## EXPERIMENTAL SECTION

### Materials

Synthesis of THPA :
All reagents used were dried and purified by distillation before use.
HCl-gas was bubbled into a solution of 50.4 g (54 ml ; 0.6 mole) of dihydropyran in 150 ml of anhydrous diethyl ether at 0°C until no more was absorbed. After evaporation of the ether under reduced pressure at 0°C, the residue (2-chlorotetrahydropyran) was slowly added to a solution of 21.5 g (25 ml ; 0.5 mole) of ethyleneimine and 55.5 g (75 ml ; 0.55 mole) of triethylamine in 150 ml of ether at -35°C. The reaction mixture was neutralized with an aqueous solution of potassium carbonate. The ether fraction was fractionated to give 40 to 45 g of N(2-tetrahydropyranyl)aziridine (bp : 65°C/16 mm Hg).
Initiators :
$CF_3SO_3CH_3$ and $BF_3.OEt_2$ were distilled before use.
$Et_3O.BF_4$ was purified as described earlier (5).

### Polymerization procedure

1.98 g (2 ml ; $15.6x10^{-3}$ mole) THPA was introduced in a glass vial of 50 ml against a current of dry nitrogen. After cooling the monomer to -65°C, 4.34 mg (3µl ; $2.65x10^{-5}$ mole) of methyl triflate was added. The temperature of the cooling bath was kept at -50°C for 20 minutes. Then it was allowed to warm up slowly. After 30 minutes, the polymerization mixture could no longer be stirred, and solidified as a glassy transparent product. 50 ml of 0.1 N HCl was added at room temperature. After 12 hours, 25 ml of 1 N NaOH was added and the white precipitate was filtered off on a G3-glass filter, washed with distilled water until the filtrate was neutral and free of NaCl, and dried under reduced pressure at 40°C. Yield : 0.61 g (92 %).

### Instruments

$^{13}C$-NMR spectra were recorded on a Bruker WH 200 apparatus.
DSC measurements were done by means of a Perkin-Elmer DSC-2C instrument.
A Chromatix KMX-6 light scattering instrument was used to determine weight average molecular weights of the LPEI samples in methanol.

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