Copolymerization without initiator of 1-(2-hydroxyethyl)aziridine and acrylamide

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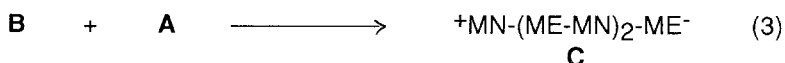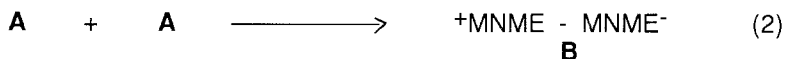
SUMMARY

1-(2-Hydroxyethyl)aziridine as nucleophilic monomer was copolymerized in the absence of an initiator under various experimental conditions with acrylamide as electrophilic monomer. All copolymers were characterized by elemental analysis, IR, and ^{1}H-NMR spectroscopy. The viscosity measurements showed that the copolymers behave as polyelectrolytes. The copolymer composition was determined from elemental analysis and ^{1}H-NMR spectra.
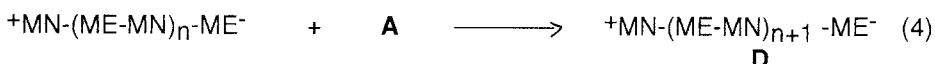
INTRODUCTION

The process of copolymerization usually needs an initiator, catalyst or high energy radiation, but there have been reports on a class of co- and terpolymerizations which occur without any added catalyst or initiator (1-4). In this type of copolymerization reaction between a monomer with nucleophilic reactivity (MN) and other that possesses electrophilic reactivity (ME) a zwitterion **A** is produced,

$$MN \ + \ ME \ \longrightarrow \ ^+MN - ME^- \qquad (1)$$
$$\mathbf{A}$$
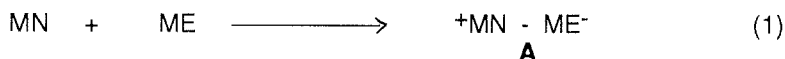
which is the key intermediate responsible for initiation as well as for propagation. The following general scheme shows the growth of the "genetic zwitterion" **A** into oligo- and macrozwitterions.

$$\mathbf{A} \ + \ \mathbf{A} \ \longrightarrow \ ^+MNME - MNME^- \qquad (2)$$
$$\mathbf{B}$$

$$\mathbf{B} \ + \ \mathbf{A} \ \longrightarrow \ ^+MN\text{-}(ME\text{-}MN)_2\text{-}ME^- \qquad (3)$$
$$\mathbf{C}$$

In general:

$$^+MN\text{-}(ME\text{-}MN)_n\text{-}ME^- \ + \ \mathbf{A} \ \longrightarrow \ ^+MN\text{-}(ME\text{-}MN)_{n+1}\text{-}ME^- \qquad (4)$$
$$\mathbf{D}$$

In connection with that, spontaneous copolymerizations have been reported for nucleophilic monomers as cyclic iminoethers, aziridines, with electrophilic

monomers as α,β-unsaturated acids (5-9), lactones (10-13), sulfones (14), maleimide derivatives (15-19), cyclic anhydrides (20,21).

This paper reports the copolymerization of 1-(2-hydroxyethyl)aziridine, **1** as nucleophilic monomer with acrylamide, **2** as electrophilic monomer. The polyelectrolyte behavior was investigated by viscosimetry.

$$H_2C\!-\!\!-\!\!-\!CH_2$$
$$\diagdown N \diagup$$
$$|$$
$$CH_2CH_2OH$$

$$H_2C = CH$$
$$|$$
$$C = O$$
$$|$$
$$NH_2$$

1   **2**
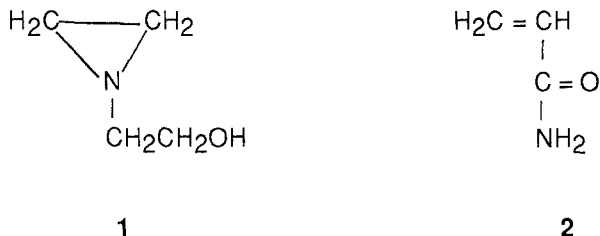
EXPERIMENTAL PART

Monomers: 1-(2-Hydroxyethyl)aziridine, **1** (from Aldrich) was purified by distillation under nitrogen and acrylamide, **2** (from Merck) by crystallization. The solvents were purified by the usual methods (22).

Copolymerization: The process was carried out in flask under N_2. Various **1** and **2** concentrations were used, keeping constant the total number of mol, in the presence of p-methoxyphenol as a radical polymerization inhibitor and 10 ml of acetonitrile as solvent. The flasks were placed in a thermostat at 50°C for a determined polymerization time. The copolymerization solutions were precipitated in diethyl ether. The copolymers were purified by reprecipitation and dried under vacuum to constant weight.

Characterization: The IR spectra were recorded on a Bruker IFS-48 spectrophotometer. The ^{1}H-NMR spectra were recorded at room temperature on a Bruker AC 250 spectrophotometer. The chemical shifts were reported (in ppm) relative to internal standard TMS. The viscosity of the copolymers was determined with an Ostwald viscometer thermostated at 30.0 ± 0.1°C using methanol as solvent.

RESULTS AND DISCUSSION

The copolymerization of 1-(2-hydroxyethyl)aziridine, **1** with acrylamide, **2** without initiator were carried out varying the initial composition between both monomers and keeping constant the total amount of the substance (0.04 mol).

All functional copolymers are soluble in water.

By means of elemental analyses the copolymer composition was determined (from the N/C ratio, see Table 1).

There is a strong dependence of the copolymers structure on the initial composition of the comonomer mixture. Table 1 shows that the relative amount of monomeric units of **1** incorporated in the copolymer is directly proportional to the relative amount of **1** in the comonomer initial mixture.

Table 1. Conditions and results of copolymerizations of **1** with **2** at 45°C in CH_3CN during 48 h.

Copolymer Nº	Initial mole ratio **1/2**	N/C ratio[a]	Copolymer composition[b] **1/2**	Yield (%)
1	3 : 1	0.310	3.1 : 1.0	96
2	2 : 1	0.318	2.0 : 1.0	98
3	1 : 1	0.332	1.0 : 1.0	99
4	1 : 2	0.352	1.0 : 2.2	92
5	1 : 3	0.360	1.0 : 3.1	88

a) and b) Obtained from elemental analysis.

Table 2 shows the influence of the copolymerization temperature and solvent on the copolymer composition and yield.

It can be concluded that there is a slight preferential increase of **1** in the copolymer by increasing the temperature. Table 2 (copolymers 7, 10, 11) also shows that the solvent polarity does not have a significant influence on the yield but the more polar solvent, CH_3CN favors the incorporation of **1** in the copolymer structure.

Table 2. Influence of the copolymerization temperature and solvent on yield and composition of the copolymer for the copolymerization of **1** with **2** during 48 h.

Copolymer Nº	Solvent (10 ml)	T (°C)	N/C[a] ratio	Copolymer composition[b] **1/2**	Yield (%)
6	CH_3CN	35	0.330	1.0 : 1.0	90
7	CH_3CN	45	0.332	1.0 : 1.0	99
8	CH_3CN	55	0.331	1.1 : 1.0	99
9	CH_3CN	65	0.329	1.2 : 1.0	99
10	C_6H_5-CH_3	45	0.338	0.8 : 1.0	85
11	$ClCH_2$-CH_2Cl	45	0.341	0.7 : 1.0	89

a) and b) Obtained from elemental analysis.

The copolymerization reaction was initially and became slower later and did not show an induction period (see Fig. 1).
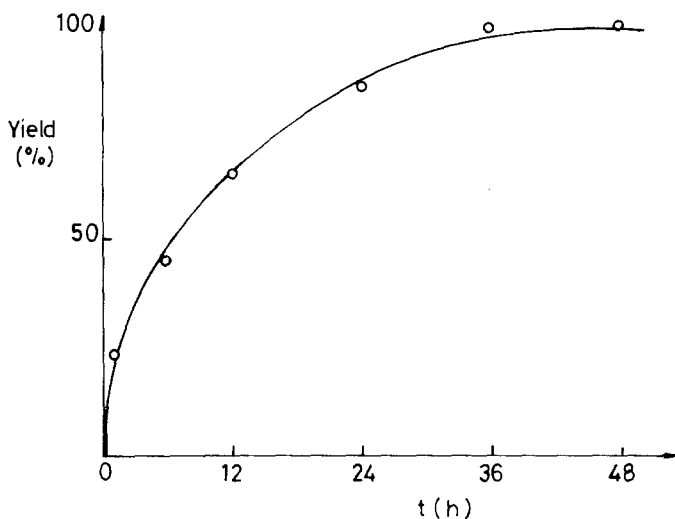
Fig. 1. Relationship between time and yield for the copolymerization of **1** with **2** (CH_3CN, 45°C).

The viscosity curves obtained are not linear, which might be due to the polyelectrolyte behavior of these copolymers. Therefore, the relation $\eta_{sp}/c = A/(1-Bc^{0.5})$, corresponding to the Fuoss-Strauss treatment (24) was applied. The results are shown in Table 3 and Fig. 2.

Table 3. Reduced and intrinsic viscosities for copolymers 1-5.

Copolymer N°	η_{sp}/c [a) $(dl \cdot g^{-1})$	$[\eta]^{-1}$ $(g \cdot dl^{-1})$	$[\eta]$ $(dl \cdot g^{-1})$
1	0.138	3.7	0.27
2	0.149	2.2	0.45
3	0.156	1.7	0.58
4	0.164	1.4	0.71
5	0.171	1.05	0.95

a) Determined in methanol at $30.0 \pm 0.1°C$, at $c = 0.5 \ g \cdot dl$.

The tendency observed is that the higher the relative amount of **2** incorporated, the higher is the intrinsic viscosity. This means that copolymer 5, rich in **2**, has the higher molecular weight.
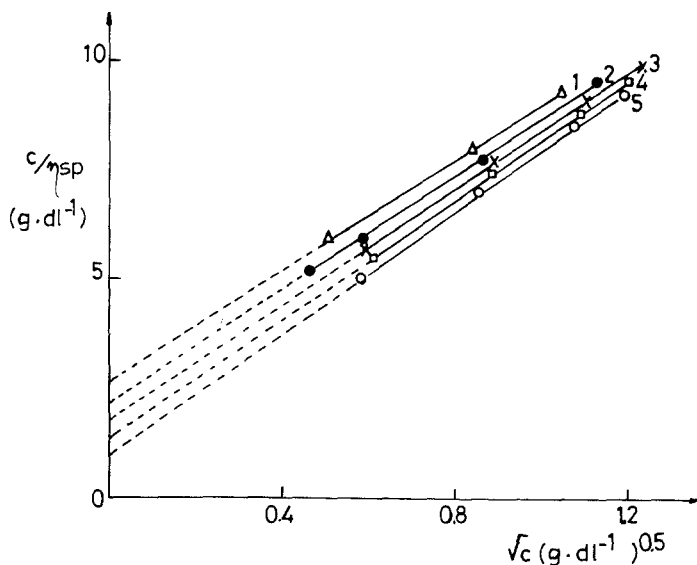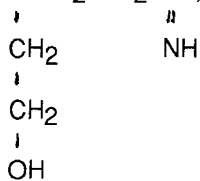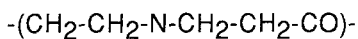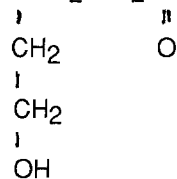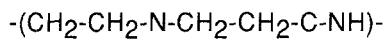
Fig. 2.   Values of c/η_{sp} as function of $c^{0.5}$. Numbers 1-5 correspond to copolymer samples in Table 1.

As the amide anion of zwitterions is an ambident anion of oxygen and nitrogen , the following two structures are possible (24):

```
-(CH2-CH2-N-CH2-CH2-CO)-              -(CH2-CH2-N-CH2-CH2-C-NH)-
            ‖                                       ‖
           CH2        NH                           CH2        O
            ‖                                       ‖
           CH2                                     CH2
            ‖                                       ‖
           OH                                      OH

            A                                       B
```

In this process a proton-transfer from **2** has occurred.

The FT-IR spectrum of copolymer (Figure 3) shows absorption bands at 1670 and 1508 cm^{-1} ($\nu_{C=O}$) from the secondary amide but not at 1585 cm^{-1} which is assigned to the $\nu_{C=N}$. These data support the formation of structure B.
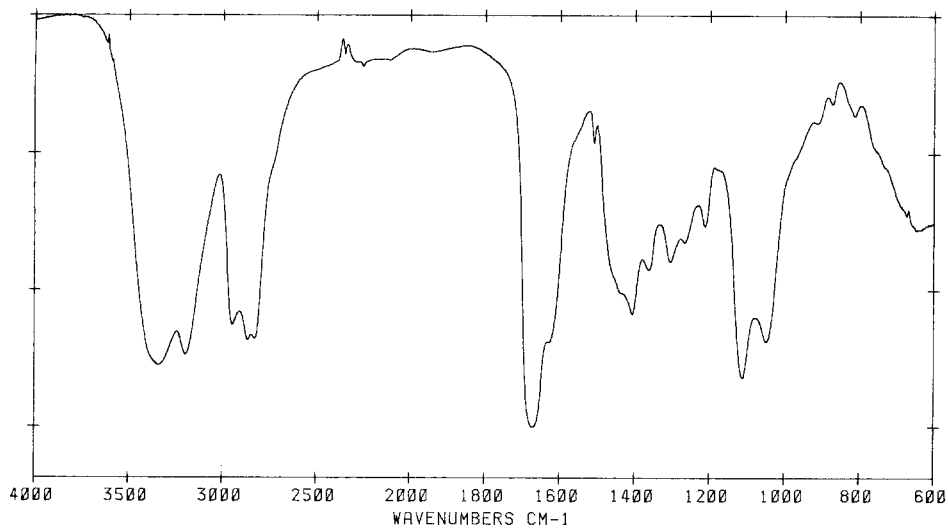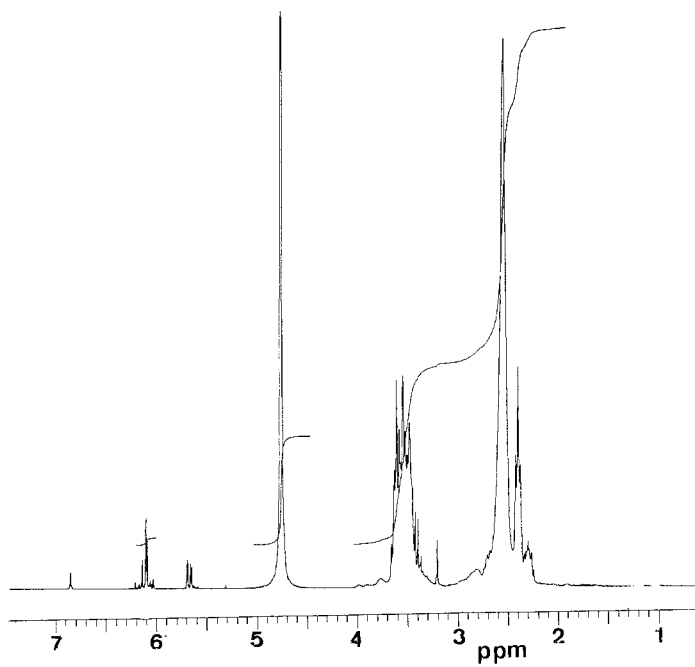
Fig. 3. FT-IR spectrum of the **1/2** copolymer, sample 3.

Fig. 4. ^{1}H-NMR spectrum of the **1/2** copolymers sample 3.

In addition, the synthesis of functional copolymers of 1-(2-hydroxyethyl)aziridine with acrylamide by spontaneous copolymerization was carried out. The copolymers with a basically amide structure behave as polyelectrolytes and showed a strong dependence of the copolymer composition on the feed monomer ratio.

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