Spontaneous copolymerization of N-(2-hydroxyethyl)ethyleneimine with maleic anhydride

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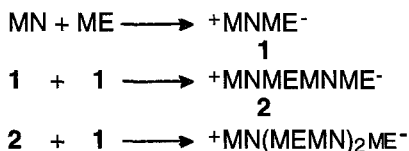
SUMMARY

The copolymerization of N-(2-hydroxyethyl)ethyleneimine (HEEI) as nucleophilic monomer and maleic anhydride (MA) as electrophilic monomer in the absence of initiator in acetonitrile was investigated. Copolymers were characterized by IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. The copolymer composition depends on the monomer ratio in the feed, determined by ^{1}H-NMR spectroscopy. The presence of MA bridges between copolymer chains was established by spectroscopic analysis. At lower temperature the yield and molecular weight of copolymers decrease as well as the MA unit content in the copolymer.
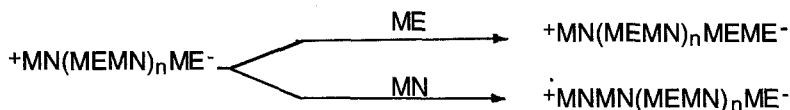
INTRODUCTION

Most of polymerization and copolymerization reactions require an initiator. However, zwitterion copolymerization occurs without initiator between a nucleophilic (MN) and an electrophilic (ME) monomer (1-20). The interaction of the monomers generates a "genetic zwitterion" $^+$MNME$^-$, which is responsible for initiation as well as for propagation.

$$MN + ME \longrightarrow \ ^+MNME^-$$
$$\mathbf{1}$$
$$\mathbf{1} \ + \ \mathbf{1} \longrightarrow \ ^+MNMEMNME^-$$
$$\mathbf{2}$$
$$\mathbf{2} \ + \ \mathbf{1} \longrightarrow \ ^+MN(MEMN)_2ME^-$$

In general:
$$^+MN(MEMN)_nME^- + \mathbf{1} \longrightarrow \ ^+MN(MEMN)_{n+1}ME^-$$

Homopropagation between a zwitterion was also proposed:

$$^+MN(MEMN)_nME^- \ \begin{array}{c} \xrightarrow{\ ME\ } \ ^+MN(MEMN)_nMEME^- \\ \xrightarrow{\ MN\ } \ ^+MNMN(MEMN)_nME^- \end{array}$$

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The latter reactions lead to statistical copolymers (10-20). Continuing our studies on non-catalyzed copolymerization through zwitterion intermediates (9-20), we now report the copolymerization of N-(2-hydroxyethyl)ethyleneimine (HEEI) as MN with maleic anhydride (MA) as ME.

EXPERIMENTAL PART

Materials: HEEI (from Aldrich) was purified by distillation under nitrogen and MA was purified by recrystallization from diethyl ether. CH_3CN (solvent) was distilled over B_2O_3 under nitrogen.

Copolymerizations: Two sets of 5 copolymerizations were carried out keeping constant the total mole number of comonomers (HEEI + MA = 0.04 mole). In a polymerization tube at a given temperature, HEEI was added under stirring on the MA solution in CH_3CN. An exothermal reaction was produced and a phase separation was observed. The polymerization was kept for 3 h. The copolymers were precipitated in diethyl ether, separated by centrifugation and dried under vacuum.

Measurements: FT-IR spectra were recorded on a Nicolet Magna-550 spectrophotometer. 250 MHz ^{1}H-NMR and 62.9 ^{13}C-NMR spectra were recorded on a Bruker AC 250-P spectrometer at 29°C in DMSO-d_6 (99.5%) with TMS as internal standard. Molecular weights of copolymers were determined with a Knauer vapour pressure osmometer in DMSO at 85°C. TG analyses were recorded on a Perkin Elmer TGA-7 thermal analyzer system. The measurements were performed under N_2 atmosphere at a heating rate of 20°C min^{-1}.

RESULTS AND DISCUSSION

The copolymerization was carried out in acetonitrile at different feed compositions, but keeping constant the total amount of comonomers (0.04 mole) (see Table I). The HEEI/MA copolymers were white hygroscopic solids.

TABLE I. Conditions and results of the copolymerization of N-(2-hydroxyethyl)ethyleneimine (HEEI) with maleic anhydride (MA) in CH_3CN at room temperature (ca. 20°C) for 3 h.

Copolymer sample number	Feed monomer mole/ratio HEEI/MA	HEEI/MA copolymer composition[b]	Yield (%)	$\overline{Mn}$[a]	Bridge MA-units (%)
1	3.0 : 1.0	2.5 : 1.0	88	4.000	5
2	1.6$_7$: 1.0	2.1 : 1.0	85	5.300	5
3	1.0 : 1.0	1.0 : 1.0	88	5.270	31
4	0.6$_7$: 1.0	0.9 : 1.0	75	5.800	30
5	0.3$_3$: 1.0	0.8 : 1.0	76	5.460	28

[a] Determined by vapour pressure osmometry in DMSO at 85°C.
[b] Determined by ^{1}H-NMR spectroscopy.

Table I shows that the HEEI copolymer composition is always higher than its concentration in the comonomers feed (except in copolymer 1). The HEEI ring is more reactive than the MA ring, which is not able to homopolymerize under these conditions. The yield is above 75%. Yields may be subject to error because the copolymers are hygroscopic.

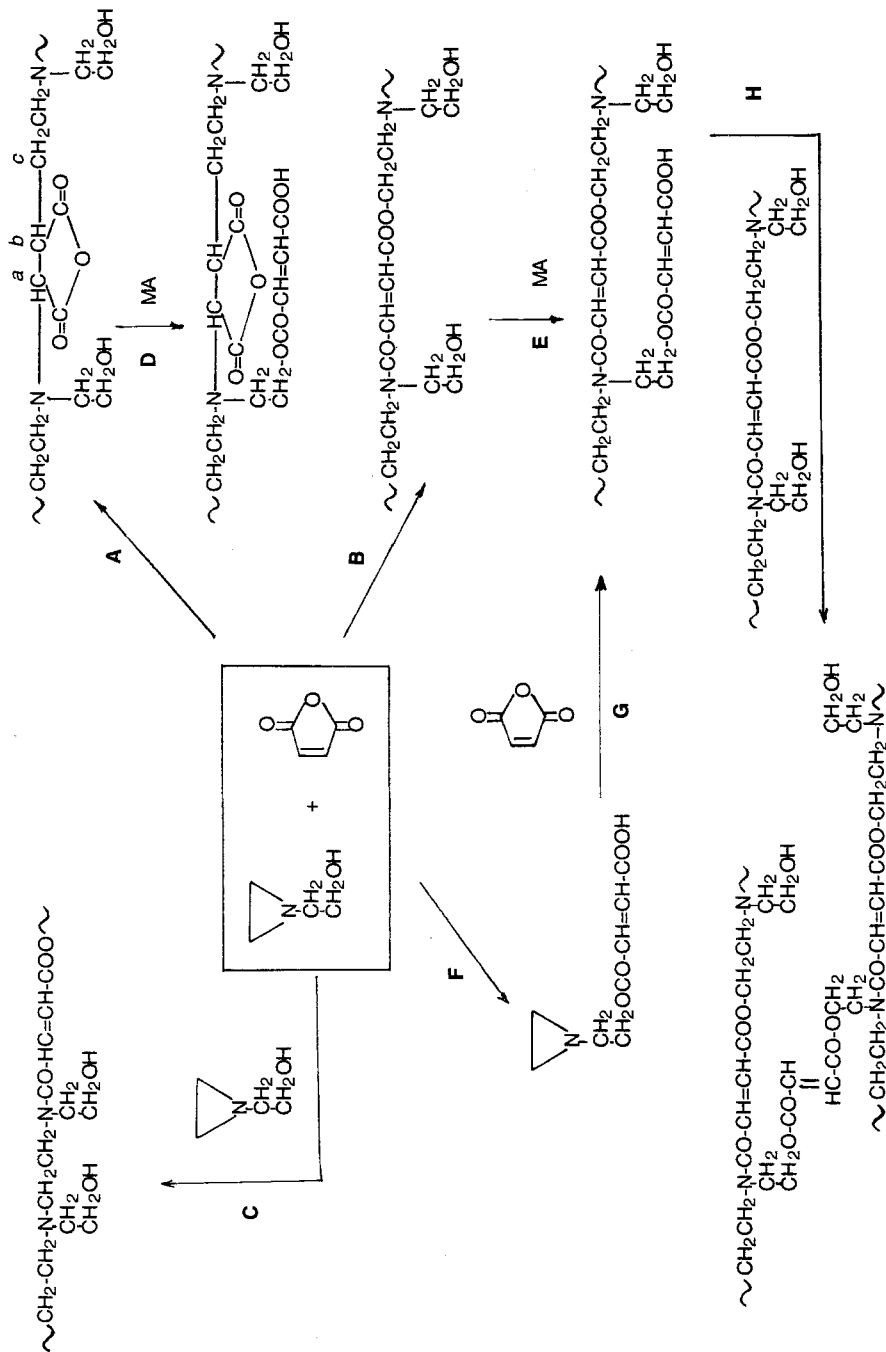The following polymeric structures are expected:

~CH₂CH₂-N

CH_2
CH_2OH

a b c
HC—CH—CH₂CH₂-N~

O=C   C=O
   O

D | MA

~CH₂CH₂-N CH_2
CH_2CH CH_2
CH_2OH CH₂-N~

CH_2
CH_2OH

O=C   C=O
   O

~CH₂CH₂-N-CO-CH=CH-COO-CH₂CH₂-N~

CH_2
CH_2OH

CH_2
CH_2OH

CH_2-OCO-CH=CH-COOH

E | MA

~CH₂CH₂-N-CO-CH=CH-COO-CH₂CH₂-N~

CH_2
CH_2OH

CH_2
CH_2OH

CH_2-OCO-CH=CH-COOH

H

A

B

~CH₂CH₂-N-CO-CH=CH-COO-CH₂CH₂-N~
CH_2
CH_2OH

CH_2
CH_2OH

~CH₂CH₂-N-CO-CH=CH-COO-CH₂CH₂-N~
CH_2
CH_2OH

CH_2OH
CH_2
HC-CO-OCH₂
CH_2
CH_2O-CO-CH
~CH₂CH₂-N-CO-CH=CH-COO-CH₂CH₂-N~

N
CH_2
CH_2OH

+

G

F

N
CH_2
$CH_2OCO-CH=CH-COOH$

C

~CH₂-CH₂-N-CH₂CH₂-N-CO-HC=CH-COO~
CH_2 CH_2
CH_2OH CH_2OH

N
CH_2
CH_2OH

DIAGRAM I

According to this diagram, path (**A**) shows the opening of the aziridine ring maintaining the MA ring, and pathway **B** with opening of both rings. By spectroscopic analysis it is possible to determine the reaction path and the probable copolymer structure. The FT-IR spectra for the copolymers **1, 3** and **5** are shown in Fig. 1. All the copolymer spectra show the presence of carbonyl groups with variable intensity between 1733 cm^{-1} and 1635 cm^{-1}. The intensity of $\nu_{(C=O)}$ signal (ester + carboxylic acid) at 1721 cm^{-1} increases as the MA units increase in the copolymer. It also shows a broadening and a displacement of the signal up to 1733 cm^{-1} for copolymer **5**. Simultaneously, the signals at 1637 cm^{-1} ($\nu_{(C=O)}$ amide + $\nu_{(C=C)}$ α-β unsaturated ester) and at 1585 cm^{-1} ($\nu_{(C=C)}$ α-β unsaturated amide) in copolymer **1** decrease in intensity relative to the preceding signal (at 1721 cm^{-1}), as the HEEI units decrease in the copolymer (from copolymer **1** to **5**). This effect is accompanied by a decrease of the signal intensity $\nu_{(OH)}$, at 3431 cm^{-1}.
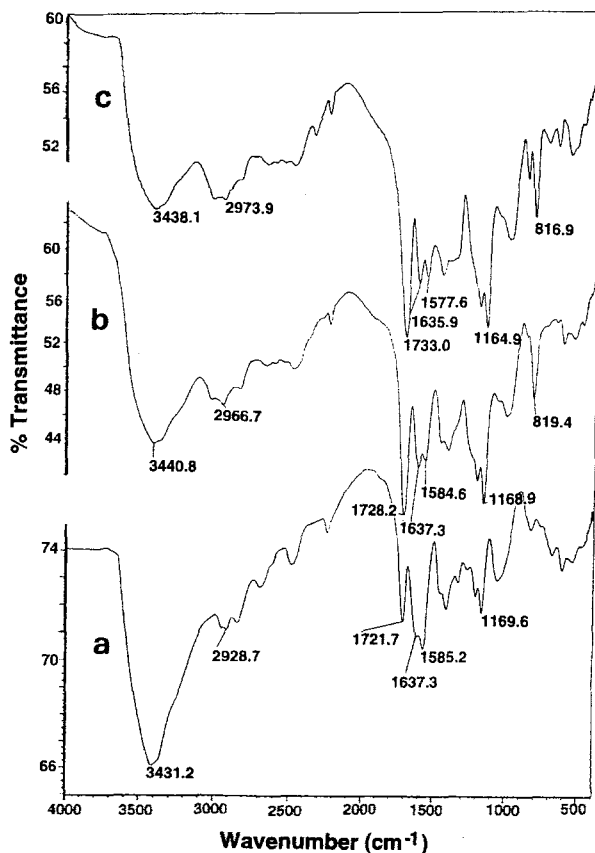

FIG. 1. FT-IR spectra of poly(N-(2-hydroxyethyl)-ethyleneimine-*co*-maleic anhydride) samples: **1** (a), **3** (b) and **5** (c).

The presence of amide and ester linkages indicates that the reaction occurred through pathway **B**. However, it should be possible to obtain a structure where both pathways **A** and **B** occur simultaneously.

If the copolymerization occurs only through pathway **A**, the aliphatic tertiary carbons "*a*" and "*b*" must be present, which in the[13]C-NMR(DEPT) spectra should absorb at 47 ppm and 35 ppm (calculated chemical shifts), respectively. However, the DEPT spectra show the total absence of tertiary aliphatic carbons. The signal for the methylene carbons "*c*", which must absorb around 30 ppm, is also absent. This allows to conclude that the polymerization did not occur through the MA double bond (pathway **A**). However, these spectra show signals between $\delta = 124$ ppm and $\delta = 138$ ppm corresponding to tertiary olefinic carbons, indicating an opening of both rings. At low field the spectra also show the signals from the carbonyl carbons: $\delta = 164.5$ ppm (m, amide); $\delta = 166\text{-}167$ ppm (m, acid) and for ester carbonyl carbon a multiplet between $\delta = 167.1$ ppm and $\delta = 167.3$ ppm and a singlet at $\delta = 167.2$ ppm. These signals corroborate the conclusions by FT-IR spectroscopy.

The 250 MHz ^{1}H-NMR spectrum shows the olefinic protons between $\delta = 6.7$ ppm and $\delta = 5.5$ ppm; CH_2COO protons centered at $\delta = 4.2$ ppm; methylene protons (CH_2OH) centered at $\delta = 3.6$ ppm; amide methylene protons ($CH_2\text{-}N\text{-}CO$) centered at $\delta = 3.15$ ppm and methylene amine protons ($CH_2\text{-}N\text{-}CH_2$) centered at $\delta = 2.85$ ppm. The signal at $\delta = 2.45$ ppm corresponds to the DMSO-d_6 (99.5%) used as solvent and lock. For all copolymers the intensity of each peak varied according to the copolymer composition.
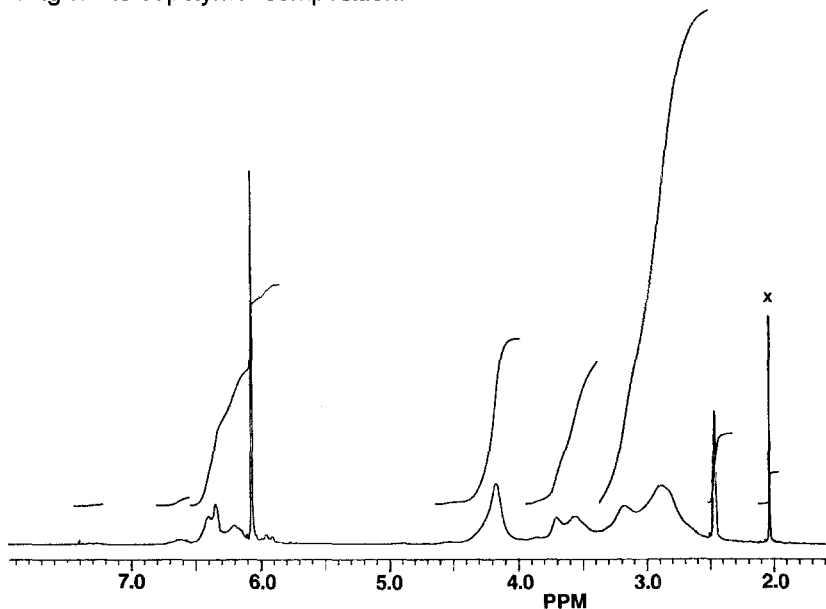

FIG. 2.   ^{1}H-NMR spectrum of the poly(N-(2-hydroxyethyl)ethyleneimine-*co*-maleic anhydride), sample **3** (250 MHz, DMSO-d_6, 29°C, TMS, x = solvent, CH_3CN)

From the relationships of the unit areas for the olefinic protons (δ = 6.7 - 5.9 ppm) and those for the aliphatic protons (δ = 4.5 - 2.2 ppm) it is possible to calculate the ratio of both monomers in the copolymer.

According to the data shown in Table I, the copolymers **1** and **2** are richest in HEEI (see pathway **C**). As the MA does not homopolymerize, the highest incorporation of MA in the copolymers **4** and **5** may be explained by esterification of the hydroxyethyl side groups of HEEI (see pathway **E**).

The ^{1}H-NMR spectrum of copolymer **3** (see Fig. 2) showed a singlet at 6.15 ppm corresponding to equivalent protons -CH=CH-.

The ^{1}H-NMR spectra of HEEI and MA recorded under the same experimental conditions showed a singlet at different chemical shifts (δ = 7.45 ppm and 6.33 ppm respectively). After reprecipitation copolymer **3** did not show the absence of the signal at δ = 6.15 ppm which implies that this signal is not produced by the rest of monomers (or very low molecular weight compounds) but from the copolymer.
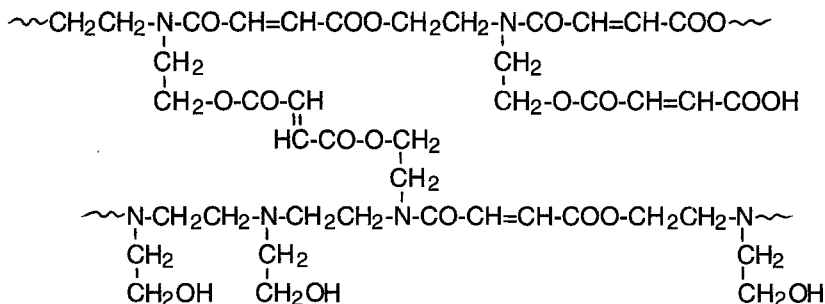
The δ = 6.15 ppm singlet is not formed by pathway **E** because this copolymer structure has no equivalent olefinic carbons. However, if a new esterification is considered between the -COOH side groups formed by pathway **E** and the pendent -CH$_2$CH$_2$OH (see pathway **H**), two equivalent olefinic protons responsible of the singlet at δ = 6.15 ppm, are obtained. This esterification is favoured by the exothermal reaction and the catalyst effect of -COOH groups.

The -N-CH$_2$CH$_2$-OOC-HC=CH-COO-CH$_2$CH$_2$-N- bridge has also two equivalent olefinic carbons and carbonyl carbons easily assignable, which should appear as singlets (but no olefinic and carbonyl carbons of the backbone, where the signals depend on the copolymer sequence structure which are absorbed as multiplets). Thus, the ^{13}C-NMR of all the copolymers showed, among other signals, a singlet at δ = 135.4 ppm (C=C α,β-unsaturated ester) and another at δ = 167.2 ppm corresponding to the carbonyl carbon of the ester. These results support a copolymer formed by pathway **H**.

According to this analysis, the structure of copolymer **3** (copolymer composition 1.0 : 1.0) is not alternating , but it is formed principally by short chains of the copolymer richest in HEEI linked by MA-bridges.

The relationships between the proton area of the singlet at δ = 6.15 ppm concerning the total area of the olefinic protons (see Fig. 2) can be used to determine the percentage of MA units that are acting as bridges between the polymer chains (see Table I).

The following copolymer structure is in agreement with the spectroscopic data:

~~CH₂CH₂-N-CO-CH=CH-COO-CH₂CH₂-N-CO-CH=CH-COO~~ structure:

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〜〜CH2CH2-N-CO-CH=CH-COO-CH2CH2-N-CO-CH=CH-COO〜〜
            |                        |
            CH2                      CH2
            |                        |
            CH2-O-CO-CH              CH2-O-CO-CH=CH-COOH
                     ‖
                  HC-CO-O-CH2
                          |
                          CH2
                          |
    〜〜N-CH2CH2-N-CH2CH2-N-CO-CH=CH-COO-CH2CH2-N〜〜
        |         |                            |
        CH2       CH2                          CH2
        |         |                            |
        CH2OH     CH2OH                        CH2OH
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The alternative pathways **F** and **G** to obtain this type of copolymer is considered less probable, because the opening of a strain ring of HEEI is mostly favoured than MA ring.

To study the temperature effect on the copolymer composition, a set of copolymerization reaction of both monomers at 0°C under the same conditions was carried out.

TABLE II. Conditions and results of the copolymerization of HEEI and MA in acetonitrile at 0°C for 3 h.

Copolymer sample number	Feed monomer mole/ratio HEEI/MA	HEEI/MA copolymer composition	Yield (%)	Mn[a]	Bridge MA-units (%)
6	3.0 : 1.0	5.0 : 1.0	77	3.600	6
7	1.6₇ : 1.0	1.6 : 1.0	86	3.200	6
8	1.0 : 1.0	1.2 : 1.0	82	3.400	13
9	0.6₇ : 1.0	1.2 : 1.0	70	3.500	14
10	0.3₃ : 1.0	1.2 : 1.0	51	4.100	25

a)Determined by vapour pressure osmometer in DMSO at 85°C.

In general, copolymers **6-10** are richer in HEEI than copolymers **1-5** because a decrease of the temperature produces a decrease in MA reactivity. A decrease of the MA-bridges (%) is also observed, being very noticeable for copolymers **8, 9** and **10**. These copolymers have the same copolymer composition but the percentage of the MA-bridges, increases due to an increase of the MA concentration in the feed. For this series, as expected, the yield and the molecular weight are slightly lower than those carried out at room temperature (ca. 20°C).

The copolymerization mechanism is analogous to that proposed by the authors (21,22) for other copolymerization systems.

Thermal analysis

The thermal behaviour showed that the thermal stability Ea increases as the MA-bridges decrease (see Table III). TDT₁₀% decreased as the HEEI unit contents decreased in the copolymer but there is no an important change on the TDT₅₀% for all the copolymers, these values are lower than those of HEEI and phthalic anhydride (19), due to an aromatic conjugation of the ester and amide linkages. The thermal degradation occurs according to a zero order reaction (21). This

implies that the sample geometry is such that the diffusions of the volatiles to the sample surface and their evaporation from the sample surface are rate-controlling factors.

TABLE III. Activation energy and thermal decomposition temperature, TDT, of HEEI/MA copolymers.

Copolymer sample number	$TDT_{10\%}$[a] (K)	$TDT_{50\%}$[b] (K)	Activation energy (Kcal/mol)	Copolymer composition HEEI/MA
1	495	584	11.27	2.5 : 1.0
2	483	586	8.30	2.1 : 1.0
3	461	587	3.83	1.0 : 1.0
4	454	589	4.05	0.9 : 1.0
5	425	573	2.40	0.8 : 1.0

[a] [b] Temperatures that occur at 10% and 50% of weight-loss respectively.

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