

Copolymerization without initiator of *N*-(2-hydroxyethyl)ethyleneimine with succinic anhydride

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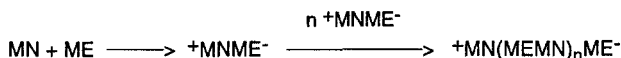
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SUMMARY

Copolymers of *N*-(2-hydroxyethyl)ethyleneimine and succinic anhydride without initiator were prepared under different experimental conditions. The composition of the copolymers was determined by elemental analyses and ¹H-NMR spectroscopy. From the results of FT-IR and ¹H-NMR spectroscopy a scheme of copolymerization via zwitterion is presented which includes an esterification reaction of the pendant hydroxylic groups.

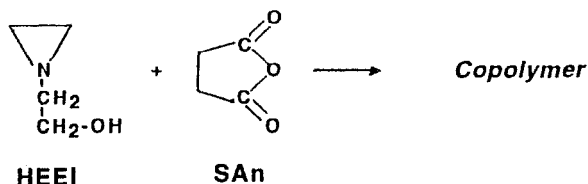
INTRODUCTION

Most of the polymerization reactions require an initiator, catalyst or high energy radiation. However, in the last years a copolymer series has been obtained without initiator by the so-called "spontaneous copolymerization via zwitterion" or "no-catalyst copolymerizations via zwitterion intermediates" (1-11). In this case, the interaction between monomers is essential. One monomer must have electrophilic reactivity (ME) and the other must possess nucleophilic reactivity (MN). The interaction of the species generates an ionic species ⁺MNME⁻ which is the key intermediate responsible for initiation as well as for propagation.



If the growth reaction involves only "polyaddition" and "polycondensation" reactions, an alternating copolymer is obtained. It is also possible that a lateral reaction may occur by interaction of the zwitterionic species with the monomer, MN or ME, originating the production of statistical copolymers.

This paper reports the copolymerization of *N*-(2-hydroxyethyl)ethyleneimine (HEEI) as nucleophilic monomer with succinic anhydride (SAn) as an electrophilic one.



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EXPERIMENTAL PART

Reagents: SAn (Merck) and HEEI (Aldrich) were purified by recrystallization (twice) from chloroform and by distillation under N_2 respectively. The solvents were dried by usual methods (12).

Copolymerization. A set of 5 copolymerizations were carried out according to the following technique, varying the feed monomer ratio but keeping constant the total amount of monomers (0.04 ml). In a polymerization flask the SAn moles were dissolved in 30 ml of CH_3CN under N_2 and stirring. The flask was placed in an ice/water bath. HEEI was added dropwise yielding phase separation. After 1h diethyl ether was added. The mixture was centrifuged. The polymeric material was dried in vacuum to constant weight. A fraction of copolymer was purified by dissolution in DMSO and reprecipitation in CH_3COCH_3 .

Measurements: The film-copolymer FT-IR spectra were recorded on a Magna Nicolet 550 spectrophotometer. 1H -NMR spectra were recorded on a Bruker AC 250-P spectrometer at 29°C. The thermal analyses were carried out in a STA 625 Thermobalance (Polymer Laboratories) in N_2 at heating rate of 10°C/min. The molecular weights were determined by a Vapor Pressure Osmometer (Knauer) in DMSO at 85°C.

RESULTS AND DISCUSSION

In Table 1 the polymerization conditions of HEEI/SAn and some properties of the copolymers are summarized.

Table 1. Copolymerization of HEEI with SAn in CH_3CN , copolymer composition and \bar{M}_n .

N ^o	Feed Monomer ratio HEEI/SAn	Yield (%)	N/C ^a	\bar{M}_n	Copol. Composition HEEI/SAn	
					from N/C	by 1H -NMR
1	0.030 : 0.010	50 ^b	0.1890	6194	1.84 : 1.0	4.2 : 1.0 ^c
2	0.025 : 0.015	48 ^b	0.1713	5836	1.36 : 1.0	1.4 : 1.0
3	0.020 : 0.020	24 ^b	0.1589	3669	1.20 : 1.0	1.4 : 1.0
4	0.015 : 0.025	21 ^b	0.1545	3710	1.13 : 1.0	1.2 : 1.0
5	0.010 : 0.030	14 ^b	0.1416	3295	0.94 : 1.0	1.0 : 1.0

a) From elemental analyses

b) Weight of copolymer before reprecipitation

c) Soluble fraction of copolymer

This table shows that the yield is low and decreases as the concentration of SAn increases. In general, the copolymer compositions from elemental analyses (N/C ratio) are slightly lower than those from 1H -NMR spectra. This may be attributed to DMSO (solvent) occluded in copolymer which is very difficult to remove (b.p. 197°C), and possesses a lower hydrogen content than HEEI. In both cases the copolymer composition depends on the feed comonomer ratio. For copolymer 1, the copolymer composition is 4.2:1.0 because only the soluble fraction of the copolymer was analyzed spectroscopically.

The \bar{M}_n determined by vapor pressure osmometry showed that as feed monomer rate is richest in SAn, the \bar{M}_n decreases. This tendency is corroborated by viscosity measurements giving typical polyelectrolyte curves.

The FT-IR spectra of the copolymers show disappearance of signal $\nu_{(C=O)}$ from anhydride at 1800 cm^{-1} and the presence of the signals $\nu_{(C=O)}$ of ester at 1730 cm^{-1} and amides I and II at 1640 and 1580 cm^{-1} respectively. This means that either the anhydride molecule or HEEI were opened (see Fig. 1). Besides, FT-IR spectra indicate that the signal of $\nu_{(C=O)}$ from ester is stronger than the signals of amide I and amide II as the polymers become rich in SAn.

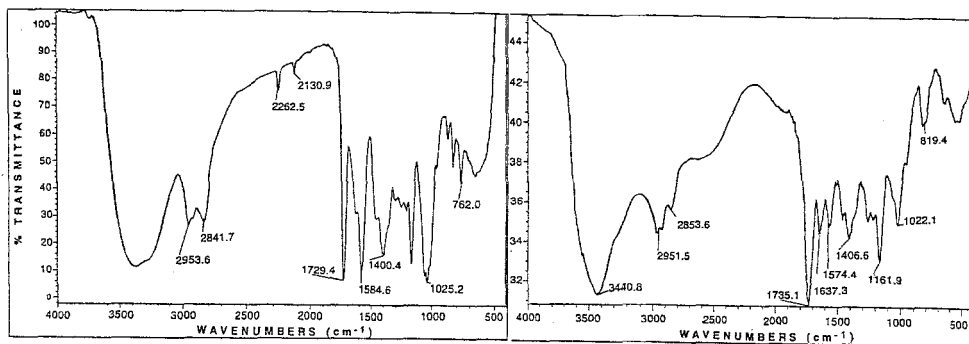


Figure 1. FT-IR (film) of the copolymers **1** and **5**.

The $^1\text{H-NMR}$ spectrum of copolymer **3** is shown in Figure 2.

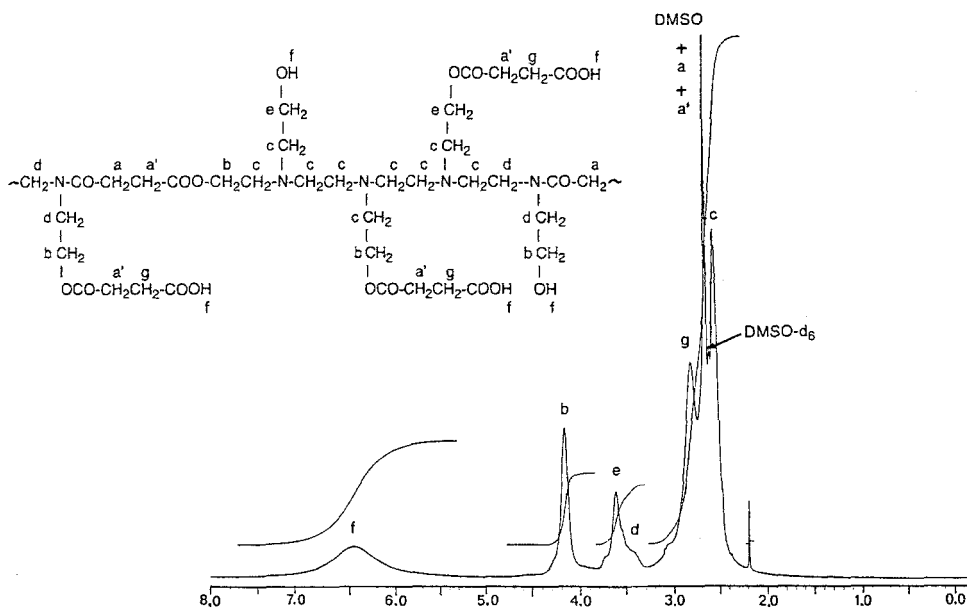
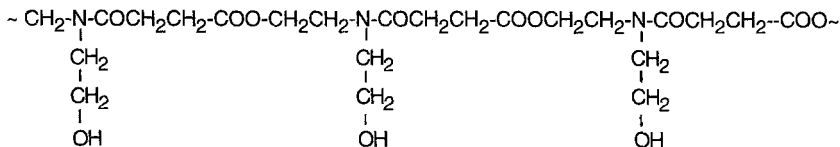


Figure 2. $^1\text{H-NMR}$ spectrum of copolymer **3**. (250 MHz, 29°C , DMSO-d_6).

The analyses of the spectra of Figure 2 show the presence of amine protons ($\text{CH}_2\text{-N-CH}_2$) at $\delta = 2.5$ ppm (proton **c**), methyl protons from DMSO- d_6 at $\delta = 2.58$ ppm, methylene protons CH_2COOH (protons **a**) and methylene protons NCOCH_2 (proton **a'**) at $\delta = 2.6$ ppm together with the protons of DMSO. The methylene protons CH_2COOH at $\delta = 2.7$ ppm (protons **g**), amide protons ($\text{CH}_2\text{-N-CO}$) between $\delta = 3.3$ and 3.5 ppm (protons **d**), methylene protons CH_2OH at $\delta = 3.6$ ppm (protons **e**), methylene protons COOCH_2 at $\delta = 4.13$ ppm (protons **b**) and the protons **f** at $\delta = 6.45$ ppm correspond to the acid and hydroxyl protons.

The signal of the protons **a** acid **a'** was observed in the spectra of the copolymers obtained without reprecipitation in DMSO. The assignment of the signal in the $^1\text{H-NMR}$ spectra was carried out considering the chemical shifts of poly(HEEI) (13), poly(ethyleneimine-*co*-succinic anhydride) (10) and analogous low molecular weight compounds (14). For example, the $^1\text{H-NMR}$ spectrum of poly(HEEI) in D_2O shows the presence of the amine protons at $\delta = 2.65$ ppm and the signal of CH_2OH at $\delta = 3.6$ ppm (13). Due to that the anhydrides do not homopolymerize under these conditions, SAN by reacting with HEEI by ring opening yields a COOCH_2 linkage where protons are absorbed at $\delta = 4.13$ ppm and being proportional to the incorporated concentration of SAN in the copolymer without considering the SAN end unit of the main chain.

If a HEEI/SAN alternating copolymer structure is analyzed



it is observed that for each SAN unit incorporated two protons COOCH_2 and 4 protons $(\text{CH}_2)_2\text{-N-CO}$ are produced. According to that, there is the same concentration of protons COOCH_2 (signal **b** at 4.13 ppm) and protons CH_2OH and the double of the protons $(\text{CH}_2)_2\text{N-CO}$. As these last types of protons have similar chemical shifts, the relation 1:3 is expected for the COOCH_2 :[$\text{CH}_2\text{OH} + (\text{CH}_2)_2\text{NCO}$] signals. Moreover, in this structure there is no evidence of amine protons, implying the absence of the signal at $\delta = 2.5$ ppm. This signal is produced only if homodyads of HEEI in the copolymer structure exist.

Table 1 shows that the composition of HEEI/SAN copolymer **3**, is 1.3:1.0. However, the intensity of the signals **e** + **d** is lower than signal **b** as it is observed in Figure 2. That means that almost all hydroxyl protons from CH_2OH are esterified by SAN and besides there is a small amount of amide bonds. This implies that the homopropagation reaction of HEEI is favoured with respect to heteropropagation. As the protons CH_2OH are esterified, they decreased the signal of CH_2OH at $\delta = 3.6$ ppm and increased the signal of the protons COOCH_2 at $\delta = 4.13$ ppm corroborating that for the copolymers with a high degree of

esterification (copolymers 3 and 5), the carboxyl:amide ratio is increased with respect to those copolymers with a lowest degree of esterification (copolymers 1 and 2). It was confirmed by FT-IR spectroscopy that the stretching signals ($\nu_{C=O}$) for amide I and II decreased as the stretching signal ($\nu_{C=O}$) of ester and carboxylic group included basically at the side chain of copolymers increased. The presence of ester and carboxylic acid groups may explain the broadening of the signal at 1735.4 cm^{-1} (see Fig. 1b). Thus, if from the area of signal **b** half of the area of signal **d** is subtracted and then added to the area of protons **e**, the concentration of HEEI unit is obtained. This value may be compared with the area of the signal of protons **b** as it has the same ponderation and it is proportional to the concentration of SAN units. According to this method the copolymer compositions were calculated (see Table 1). The esterification of CH_2OH group from HEEI unit was previously reported for other systems (8,11).

Thermal Analyses

Thermograms of copolymer 2, reprecipitated in DMSO and without reprecipitation are shown in Figure 3.

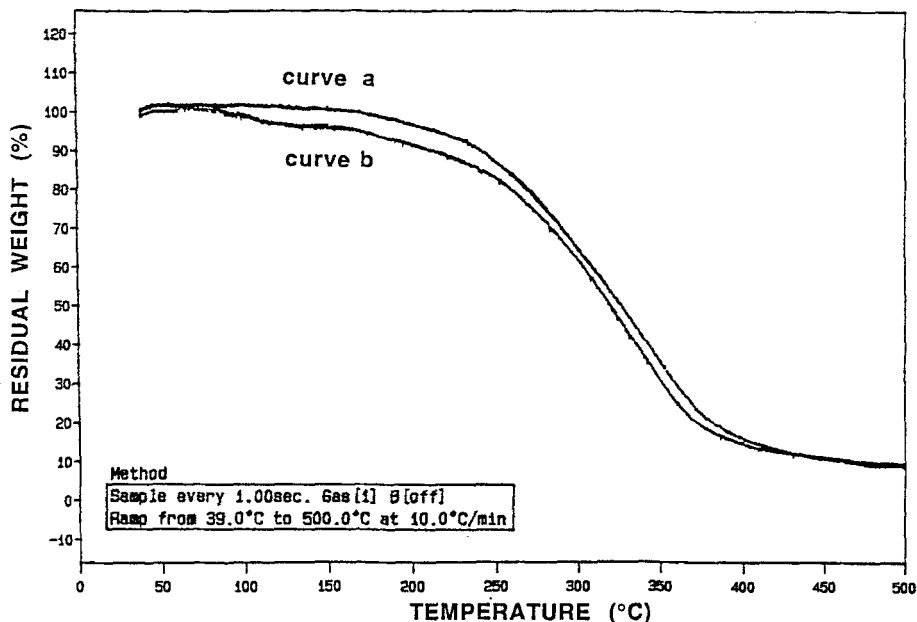
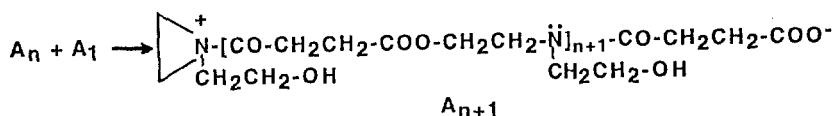
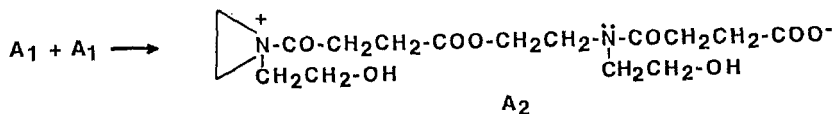


Figure 3. Thermograms of copolymer 2, without reprecipitation (a) and with reprecipitation in DMSO (b). Heating rate: $10^\circ\text{C}/\text{min}$, N_2 , weight of sample: 1.2-1.6 mg.

The stability of the reprecipitated copolymer (b) is slightly lower than that without reprecipitation (a). This indicates that the acetone-soluble copolymer fraction which was eliminated included thermally somewhat more stable fractions. Curve (b) shows that around 200°C a significant weight loss occurs due to occluded DMSO.

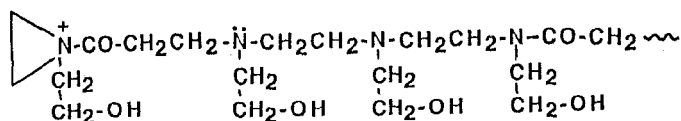
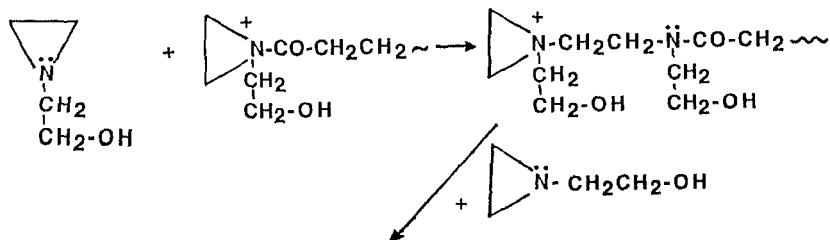
MECHANISM

HETEROPROPAGATION REACTION

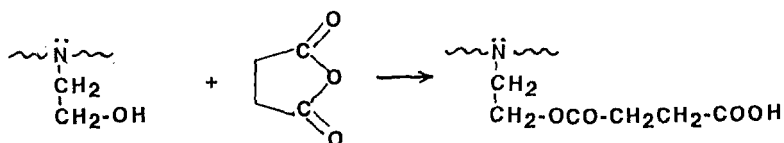


$$n \geq 2$$

HOMOPROPAGATION REACTION



ESTERIFICATION REACTION



Possible Mechanism

According to the data a mechanism "via zwitterion" is proposed.

According to the intensity of the amide protons signal in $^1\text{H-NMR}$ spectra we conclude that there is a low concentration of SAN units in the main chain. Moreover, the low intensity of the CH_2OH signals regarding the protons COOCH_2 , indicates a high degree of esterification in the side chain. This means that once the genetic zwitterion is produced, this propagates preferentially by homopropagation of HEEI yielding a polymeric chain with a major concentration of amine bonds, and hence causing the esterification of the pendant hydroxyl groups.

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