

Copolymerization via Zwitterion
7. Succinic Anhydride with 2-Ethyl-2-Oxazoline

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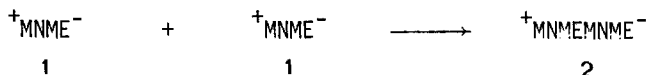
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SUMMARY

Copolymers of 2-ethyl-2-oxazoline (ETOX) and succinic anhydride (SAN) in the absence of an added initiator were synthesized at 60 °C in acetonitrile and in bulk. The statistical copolymers are rich in ETOX, and they are partially hydrolyzed by loss of the pendant group CH₃CH₂CO. Copolymer compositions and hydrolysis degree were determined by ¹H-NMR spectroscopy.

INTRODUCTION

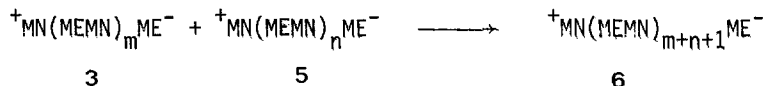
The copolymerization via zwitterion is based on a specific combination of two monomers. Thus, one monomer has nucleophilic reactivity (MN) and the other electrophilic reactivity (ME). The interaction of both monomers generates a "genetic zwitterion" (⁺MNME⁻) which functions as the key intermediate responsible for initiation as well as for propagation (1-8). Propagation is expressed by the following scheme which starts with the reaction of two moles of ⁺MNME⁻.



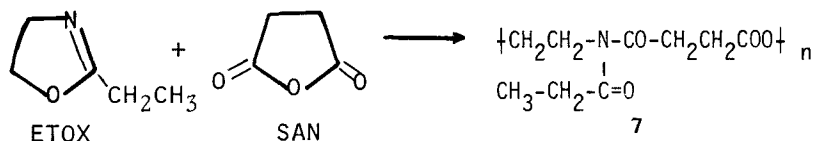
The initial propagation species 2 grows by successive reaction with 1 forming oligo- and macrozwitterions.



During the last phase of the copolymerization reactions between two macrozwitterions may occur.



This paper reports the copolymerization without initiator between 2-ethyl-oxazoline (ETOX) as nucleophilic monomer and succinic anhydride (SAN) as electrophilic monomer.



EXPERIMENTAL PART

Monomers: 2-ethyl-2-oxazoline (ETOX) (Aldrich Chemical Co.) was purified by distillation under nitrogen and succinic anhydride (SAN) (Merck) by recrystallization from chloroform.

Solvent: Acetonitrile was distilled over phosphorus pentoxide under nitrogen.

Copolymerization: A set of four copolymerizations were carried out, varying the feed molar ratio but keeping constant the total mole number (0.04) of comonomers. In a polymerization flask, under N_2 , the measured moles of SAN were dissolved in 10 ml CH_3CN just distilled (solution polymerization) and the corresponding moles of ETOX were added. The flask was kept at $60^\circ C$ for 335 h. For the bulk copolymerization, the reaction time was 143 h. The copolymer solution was added slowly to a large excess of diethyl ether. The copolymer was isolated by centrifugation, dissolved in CH_3CN , reprecipitated into ether and dried in vacuo.

Measurements: The IR (KBr) and 1H -RMN spectra were recorded on a Perkin Elmer 577 and a Varian XL-(100MHz) spectrophotometer respectively.

The viscosity of the copolymers was determined by an Ostwald viscometer thermostated at $30.0 \pm 0.1^\circ C$ using DMF as solvent.

RESULTS AND DISCUSSION

Three copolymerization reactions in acetonitrile were carried out changing the feed molar ratio of the comonomers but keeping constant the total mole number (0.04). Therefore, one run in bulk was performed using an equimolar ratio of the comonomers. The general conditions as well of yield of copolymerizations are summarized in Table 1.

Table 1. Copolymerization of ETOX and SAN at $60^\circ C$.

Copolymer	ETOX (mole)	SAN (mole)	Feed molar ratio (ETOX/SAN)	Solvent	Time (h)	Yield (%)	η_{sp}/c^*
1	0.01	0.03	1 : 3	CH_3CN	335	9.5	0.064
2	0.02	0.02	1 : 1	CH_3CN	335	16.9	0.073
3	0.03	0.01	3 : 1	CH_3CN	335	32.8	0.078
4	0.02	0.02	1 : 1	bulk	143	20.7	0.083

* The measurements were performed in N,N-dimethylformamide at $30^\circ C$ at a concentration of 0.27 g/100 ml.

The yield of the copolymerization in solution increases as the copolymer composition is richer in ETOX, but in general it is lower than for copolymerization between 2-methyl-2-oxazoline (MOX) and (SAN) (6).

The IR spectra of the four copolymer are the same and show characteristic absorption bands at 1635 cm^{-1} and 1725 cm^{-1} corresponding to the $\nu_{\text{C=O}}$ of the ester group which comes from the ring opening of SAN and $\nu_{\text{C=O}}$ amide coming from ETOX.

The copolymer composition was determined from $^1\text{H-NMR}$ spectra (see Fig. 1) according to the following suggested structure:

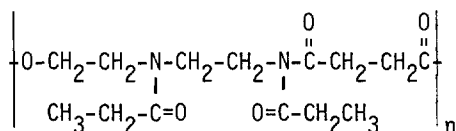


Figure 1 provided the area for the different protons which are shown in Table 2. The proton corresponding to the incorporated ETOX, (area a+b; 4H) are situated between 4.8 and 3.1 ppm; the area (c+e) integrated by methylene protons that comes from incorporated SAN (area e; 4H) and for methylene protons that come from the $\text{CH}_3\text{CH}_2\text{CO-}$ group (area c; 2H) is placed between 3.1 and 2.0 ppm. The latter area corresponds to the methyl protons from ETOX (area d, 3H) at 1.2 ppm.

To determine the integral area for each type of proton the following procedure was carried out: the area (e) of the methylene protons was calculated by subtracting the signal area between 3.1 and 2.0 ppm, the area of the methylene protons (2H) from the propionyl group corresponds to 2/3 of the area determined for protons (d).

By comparison between the areas (a+b) and (e) the comonomer ratio in the copolymer was determined.

Table 2. Proton Areas, Copolymer Composition and Hydrolysis Degree.

Copolymer	Proton Areas				Ratio ETOX/SAN Copolymer	Hydrolysis (%)
	(a+b)	(c+e)	(d)	(e)		
1	7.3	5.2	4.3 ₅	2.3	3.2/1	20.5
2	9.4 ₅	6.7	5.7	2.9	3.2/1	19.5
3	12.0	6.3	8.4	0.7	22.8/1	4.5
4	9.3	6.1	5.6	2.3 ₇	3.9/1	19.7

All copolymer are rich in ETOX. For an initial equimolar ratio of the monomers there is a preferential incorporation of ETOX in bulk, compared with the copolymerization in solution. The copolymer 1 and 2 show almost the same copolymer composition. In contrast, the relation between the areas (a+b) and (d) is not 4/3 as would be expected. This might suggest that a loss of $\text{CH}_3\text{CH}_2\text{CO-}$ occurred. The hydrolysis degree was determined from the

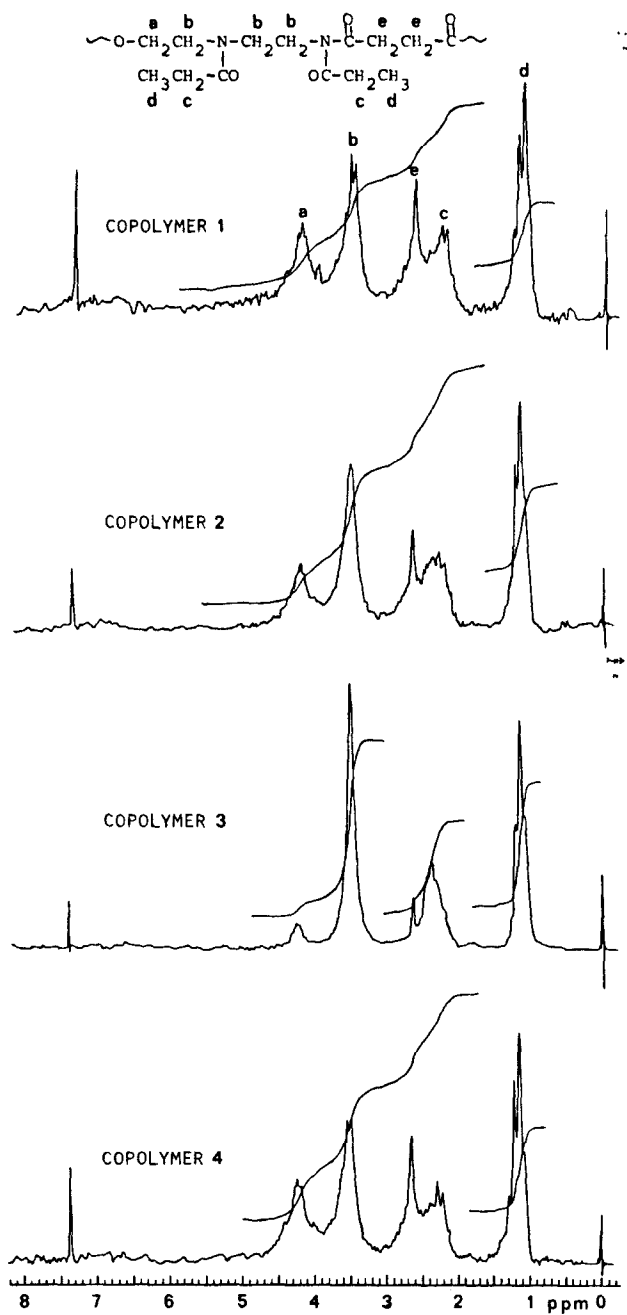


Figure 1. ^1H NMR spectra of the copolymers ETOX/SAN.
 (100 MHz, room temperature, DCCl_3 , TMS).

relationship between both areas (a+b and d). The results are shown in Table 2. The copolymers 1, 2 and 4 show a similar hydrolysis degree but for copolymer 3 it is lower. This is caused by the copolymer composition since copolymer 3 is practically a homopolymer of ETOX (22.8/1).

The loss of propionyl group is attributed to the easy hydrolysis of the imide linkages. This phenomenon has been observed previously (9,10).

The copolymerization mechanism is analogous to those proposed for other copolymerizations (6,9,10).

The study of the copolymerization of 2-ethyl-2-oxazoline with other electrophilic monomers is in progress.

ACKNOWLEDGEMENTS

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