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Copolymerization

Copolymerization via Zwitterion
3. Phthalic Anhydride and 2-Ethyl-2-Oxazoline

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SUMMARY

Copolymers of 2-ethyl-2-oxazoline and phtalic anhydride without initiator in DMF at 60 °C were synthesized. The copolymers were statistical, rich in 2-ethyl-2-oxazoline. A partial hydrolisis of pendant groups $-COCH_2CH_3$ is observed. The composition and the hydrolisis degree of the copolymers was determined by ^{1}H-NMR. A copolymerization scheme via zwitterion is proposed.

INTRODUCTION

Most all polymerization reactions require initiator, catalyst or high energy radiation. During the last few years a series of copolymerizations have been developed which occur without any added catalyst (1-6). In this new copolymerization, a zwitterion is generated by the reaction between one monomer (MN) with nucleophilic reactivity and the other (ME) that possesses electrophilic reactivity.

$$\mathrm{MN} \quad + \quad \mathrm{ME} \longrightarrow \underset{1}{{}^{+}\mathrm{MNME}^{-}}$$

Usually, the genetic zwitterion 1 is responsible for both, initiation and propagation reaction. The following general scheme shows growth of the genetic zwitterion to the macrozwitterion 2-4 which has an alternating structure.

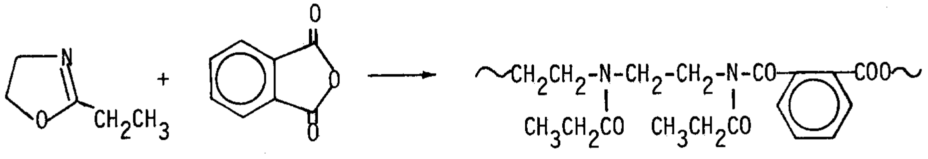
$$1 \quad + \quad 1 \longrightarrow \underset{2}{{}^{+}\mathrm{MNME - MNME}^{-}}$$

$$2 \quad + \quad 1 \longrightarrow \underset{3}{{}^{+}\mathrm{MN(ME\text{-}MN)_2ME}^{-}}$$

In general:

$${}^{+}\mathrm{MN(MEMN)_nME}^{-} \quad + \quad 1 \longrightarrow \underset{4}{{}^{+}\mathrm{MN(ME\text{-}MN)_{n+1}ME}^{-}}$$

We reported the copolymerization of 2-methyl-2-oxazoline with phtalic anhydride (7). Here is reported the copolymerization of 2-ethyl-2-oxazoline (ETOX) as nucleophilic monomer and phtalic anhydride (ANF) as electrophilic monomer to statistical copolymer, 5.



ETOX ANF 5

EXPERIMENTAL

Materials : Acetonitrile was purified by distillation over P_2O_5. 2-Ethyl-2-oxazoline (ETOX) was purified by distillation under nitrogen and the phtalic anhydride (ANF) by repeated sublimation (three times).

Copolymerization : In a glass tube, a mixture of ETOX and ANF (0.04 total mole) was dissolved in 15 ml of CH_3CN under $N_2(g)$. Then the system was kept at 60 °C for 406 h. The copolymerization mixture was poured in 250 ml of diethyl ether, obtaining a hygroscopic polymeric material. It was purified by reprecipitation and dried under vacuum.

Measurements : ^1H-NMR spectra were recorded on a Varian XL 100 spectrometer (100 MHz). The IR spectra (film) were recorded on a Perkin Elmer 577 spectrophotometer. The viscosity of the copolymers was determined by an Ostwald viscometer thermostated at 30.0 ± 0.1 °C using DMF as solvent.

RESULTS AND DISCUSSION

The copolymerization reactions were carried out at different feed molar ratios but keeping constant the total mole number (0.04). The copolymers ETOX/ANF are brown hygroscopic solids and soluble in organic solvents such as DMF, $CHCl_3$, DMSO, acetone, pyridine. The copolymerization conditions are summarized in Table 1.

Table 1. Copolymerization of ETOX/ANF at 60°C in CH_3CN by 406 h.

Copolymer	ETOX (mole)	ANF (mole)	ETOX/ANF ratio(%)	Yield (g)	Yield (%)
1	0.030	0.010	75/25	0.520	11.7
2	0.024	0.016	60/40	0.685	14.5
3	0.020	0.020	50/50	0.547	11.1
4	0.016	0.024	40/60	0.164	3.2

The copolymers were characterized by IR and ^{1}H-NMR spectroscopy, quantitative elemental analysis and viscosimetry. The four IR spectra are identical and show characteristic absorption bands at 1720 and 1640 cm^{-1} corresponding to the $\nu_{C=O}$ of the amide and carboxilic groups respectively which confirms the opening phtalic anhydride and oxazoline rings (See Figure 1).

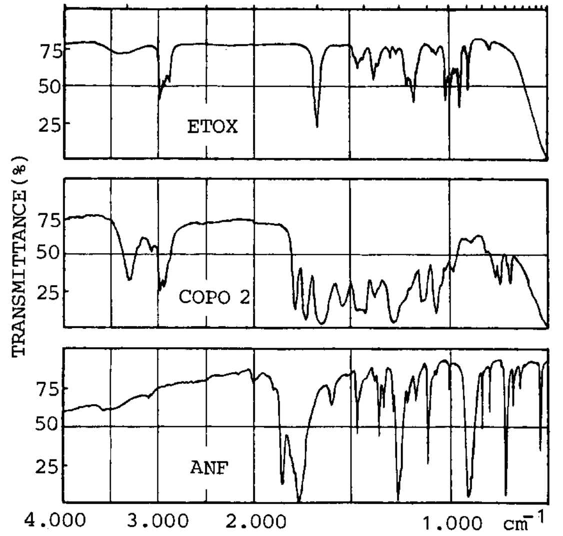


Figure 1. Infrared spectra of the a) 2-ethyl-2-oxazoline
b) copolymer ETOX/ANF (copolymer 3) and
c) phtalic anhydride.

The Figure 2 corresponds to the ^{1}H-NMR spectrum of the copolymer 2, which shows the signals 7.4 - 8.0; 6.7 - 7.0; 4.1 - 4.6; 3.1 - 4.0; 2.0 - 2.7; 0.7 - 1.3 ppm assigned to aromatic: NH; $-OCH_2-$; $-CH_2-N-CH_2-$; $-\underline{CH_2}-CH_3$ and $-CH_2-C\underline{H_3}$ protons, respectively. All the signals are present in the four spectra.

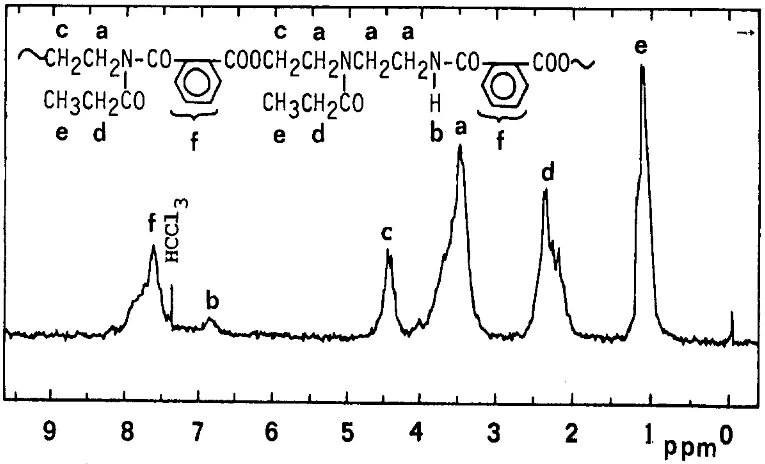
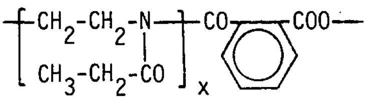


Figure 2. ^{1}H-NMR spectrum of the copolymer 2, ETOX/ANF (100 MHz, CDCl$_3$, room temperature).

The copolymer composition was determined by integration of the areas associated with aromatic (7.4 - 8.0 ppm) and methylene protons $-CH_2-CH_2N$ (3.1 - 4.0 ppm), respectively.

According to this determination the copolymer composition is statistical:



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For all molar ratios used the quantity of ETOX in the copolymer is always higher than that of ANF although the feed monomer ratio is rich in ANF (See Table 2).

The ratio of the areas for the methylene protons (CH_2CH_2N) and the methyl proton of ETOX incorporated in the polymer is lower than 4:3 suggesting that a loss of propionyl groups occurred. The broad signal at 6.7-7.0 ppm corresponding to the -NH group -which disappears by exchange with D_2O- reveals that a loss of $-CO-CH_2-CH_3$ pendant groups by partial hydrolisis in the copolymer occurred. The hydrolisis degree determined by comparing the areas of NH protons and the four methylene protons of the main chain, was 14 to 21%.

Table 2 shows that in the nearly alternating copolymer the partial hydrolisis increases by decreasing the percentage of ETOX incorporated in the copolymer. This is due to an increase in the percentage of the imide linkages, which are easily hydrolised, with a consequent loss of $-COCH_2CH_3$ groups and a correspondent decrease of the amide linkages.

Table 2. Copolymer composition and hydrolisis degree.

Copolymer	Monomer ratio ETOX/ANF	Copolymer ratio* ETOX/ANF	Hydrolisis* (%)	$\frac{\eta_{sp}}{c}$**
1	3.00 : 1.00	3.67 : 1.00	14	0.04_6
2	1.50 : 1.00	2.31 : 1.00	15	0.04_8
3	1.00 : 1.00	1.73 : 1.00	21	0.04_6
4	0.66 : 1.00	1.57 : 1.00	19	0.04_8

* Determined by ^1H-NMR (100 MHz in $CDCl_3$).

** Determined at 0.30 g/100 ml, 30 °C ± 0.1 in DMF.

The copolymer composition determined from the quantitative elemental analysis is in agreement with that determined spectroscopically, considering the hydrolisis degree (See Tables 2 and 3).

Table 3. Elemental analysis of the ETOX/ANF copolymers.

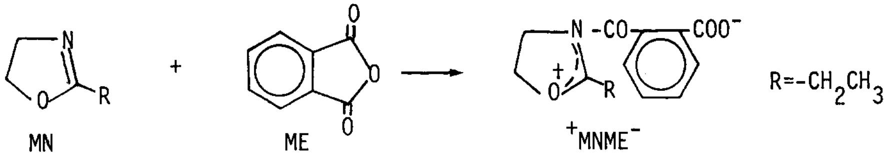
	C%	H%	N%
Found: Copolymer 1	60.77	7.40	10.31
Calc.: $(ANF)_1(ETOX\ 15\%)_{3.67}\ (H_2O)_{0.70}$	60.61	7.25	10.25
Found: Copolymer 2	61.58	6.94	8.76
Calc.: $(ANF)_1(ETOX\ 15\%)_{2.31}(H_2O)_{0.50}$	61.08	6.59	8.73
Found: Copolymer 3	61.19	6.68	7.82
Calc.: $(ANF)_1(ETOX\ 21\%)_{1.73}(H_2O)_{0.50}$	61.19	6.12	7.76
Found: Copolymer 4	62.02	6.35	7.16
Calc.: $(ANF)_1(ETOX\ 19\%)_{1.57}(H_2O)_{0.25}$	62.09	5.92	7.46

The copolymerization reaction of ETOX/ANF 3:1 in bulk at 60 °C for 63 h was carried out, to examine possible participation of the solvent on the hydrolisis degree of the copolymer. The hydrolisis degree was 27% i.e., the hydrolisis came after the copolymerization reactions occurred. The same effect was observed for 2-methyl-2-oxazoline/phtalic anhydride copolymerization (7).

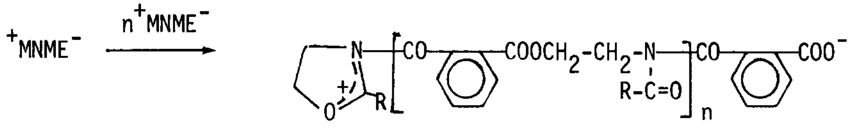
The viscosity of all four copolymers is nearly independent of the comonomer ratio.

Copolymerization mechanism.

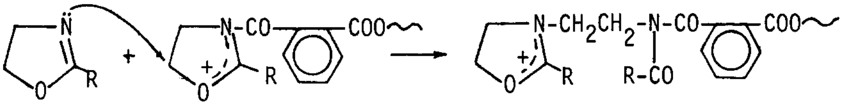
Interaction of ETOX (MN) and ANF (ME) produces the genetic zwitterion ($^{+}MNME^{-}$)



Propagation occurs by reaction of the genetic zwitterion with itself, or with larger zwitterions



or by attack of the nitrogen electron pairs of ETOX on C-5 of the oxazoline ring of a genetic or oligomeric zwitterion:



Since in all copolymerization reactions, a copolymer rich in ETOX is obtained, we can assume that the latter reaction is dominant.

The behaviour, composition and hydrolisis of ETOX/ANF copolymers is similar to those reported for the copolymerization of 2-methyl-2-oxazoline and phtalic anhydride (7).

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

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