

Copolymerization via Zwitterion

2. Phtalic Anhydride and 2-Methyl-2-Oxazoline

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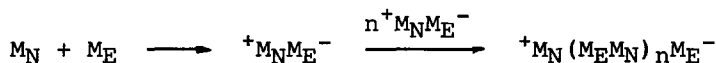
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SUMMARY

Copolymers of 2-methyl-2-oxazoline and phtalic anhydride without initiator were prepared at 60°C in DMF, CH₃CN and in bulk. The copolymers were statistical rich in 2-methyl-2-oxazoline and the -COCH₃ groups are partially hydrolyzed. The composition and the degree of hydrolysis of the copolymers were determined by ¹H-NMR. ¹³C-NMR proved that the hydrolysis did not occur during the polymerization process. A scheme of copolymerization via zwitterion is presented.

INTRODUCTION

The present paper reports the copolymerization of cyclic imino-ethers as nucleophilic (M_N) with electrophilic comonomers (M_E) to give alternating copolymers (Saegusa 1975; Saegusa et al. 1977; Balakrishnan et al. 1980; Kobayashi et al. 1982) or statistical copolymers (Rivas et al. 1983). In every case it was postulated that the polymerization takes place via zwitterion, with an intermediate ⁺M_NM_E⁻ type being formed which is responsible for the propagation.



This paper also reports the synthesis and characterization of copolymers obtained between 2-methyl-2-oxazoline (M_N) and phtalic anhydride (M_E).

EXPERIMENTAL

Materials: 2-Methyl-2-oxazoline (MOX) (Aldrich Chem. Co.) was distilled under N₂ and the phtalic anhydride (ANF) (Merck) was resublimated three times. Dimethylformamide was purified by a general method (Organikum, 1972) and acetonitrile was distilled from phosphorus pentoxide.

Copolymerization MOX/ANF: A set of 4 copolymerizations were performed, keeping constant the total mole number of comonomers (MOX + ANF = 0,04 moles). In a polymerization flask under N₂, x ANF moles were dissolved in 15 ml of DMF just distilled and (0.04-x) MOX moles were added using a syringe. The flask was introduced in a thermostated bath during 330 hours. The polymeric solution was added dropwise over 240 ml of diethyl ether and the precipitate was isolated by centrifugation, dissolved in acetone and reprecipitated over ether. The poly-

mer was dried under vacuo at 45°C.

Measurements. $^1\text{H-NMR}$ spectra were recorded on a Varian XL-100 Spectrometer (100 MHz) and Varian T60A (60 MHz). $^{13}\text{C-NMR}$ spectra were recorded on a Varian CFT-20 (20 MHz). The IR spectra (KBr) were recorded on a Perkin Elmer 577 spectrophotometer.

The viscosity of the copolymers was determined by an Ostwald viscometer thermostated at $25.0 \pm 0.1^\circ\text{C}$ using pyridine as solvent.

RESULTS AND DISCUSSION

The copolymers MOX/ANF are orange-yellowish hygroscopic solids, which can be dissolved in DMF, DMSO, pyridine and acetone, in general in polar organic solvents. The copolymerization conditions are summarized in Table I.

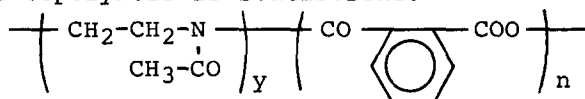
TABLE I: Copolymerizations MOX/ANF* at 60°C during 330 hours.

Exper.	MOX (Moles)	ANF (Moles)	MOX/ANF rate %	Yield (g)	Yield (%)
Copol 1	0.030	0.010	75/25	1.241	30.8
Copol 2	0.024	0.016	60/40	1.762	39.9
Copol 3	0.020	0.020	50/50	1.570	33.4
Copol 4	0.015	0.025	37.5/62.5	0.493	9.9

(*) 15 ml of DMF

The copolymers were characterized by IR and NMR spectroscopies, quantitative elemental analysis and viscosimetry. The IR spectra of the 4 copolymers are basically the same; they did not show the $\nu\text{C=O}$ of the anhydride and instead appears the characteristic frequency of the ester and amide, at 1720 cm^{-1} and 1670 cm^{-1} , respectively, which confirms the opening of the oxazoline ring and of the phthalic anhydride.

The composition of polymers was determined by integration of the aromatic proton area (7,2-8,3 ppm) and of the methylenic protons (3,8-4,8 ppm) (see Fig. 1) from $^1\text{H-NMR}$ spectra of copolymers in $(\text{CD}_3)_2\text{CO}$, and it was found that the overall composition of the copolymers is statistical.



It has been shown that the quantity of MOX in the copolymer is always higher than that of ANF, although the initial monomer ratio is rich in ANF (Table II). Therefore, in the copolymer structure, methyls of the amidic and imidic type were present. In the $^1\text{H-NMR}$ spectra in deuteroacetone, the signal for methyls is partially superposed with that of the solvent. From $^1\text{H-NMR}$ spectra, performed in $\text{C}_5\text{D}_5\text{N}$, the ratio of methylene and methylene hydrogens were determined. Evidently a partial loss of $-\text{COCH}_3$ lateral groups by hydrolysis of the copolymer occurred (Table II).

The quantitative elemental analysis was in agreement with the one estimated for these copolymers, considering the degree of hydrolysis and the composition determined spectroscopically (Table III).

To determine in which step of the copolymerization process the hydrolysis has taken place, the copolymerizations given in Table IV were performed.

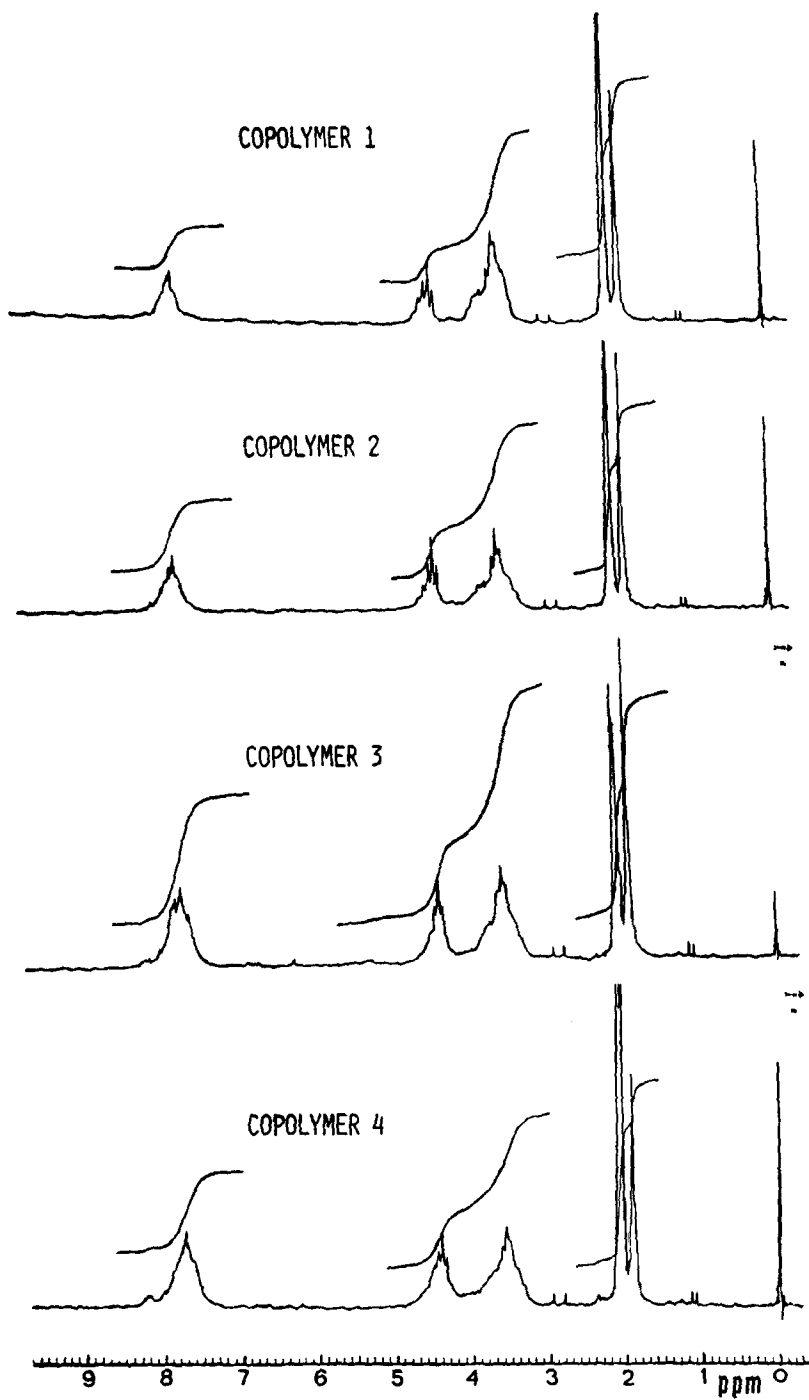


Figure 1. $^1\text{H-NMR}$ of the copolymer MOX/ANF at different molar ratios of comonomers.

TABLE II: Characterization of Copolymers

	Ratio Monom. MOX/ANF	Ratio Copo* MOX/ANF	Hydrol.** (%)	η_{sp}^{\dagger} c
Copol 1	3.0:1.0	3.5:1.0	21	0.16 ₂
Copol 2	1.5:1.0	2.2:1.0	21	0.12 ₇
Copol 3	1.0:1.0	1.8:1.0	26	0.10 ₂
Copol 4	0.6:1.0	1.7:1.0	38	0.04 ₇

(*) Determ. by $^1\text{H-NMR}$ (100 MHz) in $(\text{CD}_3)_2\text{CO}$

(**) Determ. by $^1\text{H-NMR}$ (60 MHz) in $\text{C}_5\text{D}_5\text{N}$

(†) In pyridine at 25°C at 0.20 g/100 ml

TABLE III: Elemental Analysis of Copolymers

	%C	%H	%N
Exp : Copolymer 1	54.63	6.88	10.58
Calc: (MOX 21%) 3.5 (ANF) ₁ (H ₂ O) _{1.00}	54.67	6.89	10.87
Exp : Copolymer 2	56.69	6.41	8.77
Calc: (MOX 21%) 2.2 (ANF) ₁ (H ₂ O) _{1.25}	56.35	6.20	9.11
Exp : Copolymer 3	57.08	6.35	8.55
Calc: (MOX 26%) 1.8 (ANF) ₁ (H ₂ O) _{1.00}	57.18	5.90	8.42
Exp : Copolymer 4	58.60	6.45	8.13
Calc: (MOX 38%) 1.7 (ANF) ₁ (H ₂ O) _{0.75}	58.12	5.78	8.53

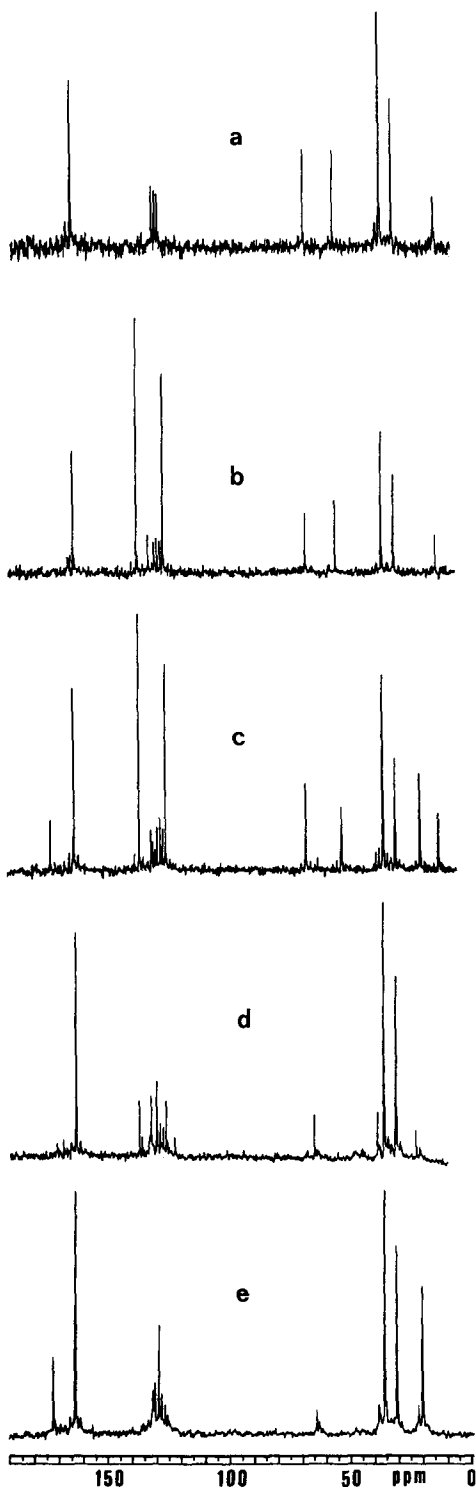
TABLE IV: Copolymerization MOX/ANF at 60°C

Experi- ment	MOX (moles)	ANF (moles)	Solvent	Time (h)	Yield (%)	Hydrol. (%)
Copol 5	0.020	0.020	20 ml CH_3CN	330	41	27
Copol 6	0.024	0.016	bulk	34	64	23
Copol 7	0.006 ₇	0.006 ₇	5 ml DMF	330	-	-

From the experiments 5 and 6 (Table IV) it was concluded that the copolymers obtained were partially hydrolyzed despite the fact the copolymerization were performed without any solvent or in dry CH_3CN instead of anhydrous DMF.

To determine if the partial hydrolysis of the copolymer has taken place during the polymerization or during the precipitation step, experiment 7 was performed in a $^{13}\text{C-NMR}$ tube. After 330 hours of copolymerization the $^{13}\text{C-NMR}$ Spectrum of the polymeric solution was directly obtained; see Spectrum "d" in Figure 2. If the hydrolysis of the copolymer has occurred during the polymerization, the signal for the methyl carbon and carbonyl carbon of CH_3COOH produced must be observed in the Spectrum.

The chemical shifts observed (in ppm) are:



DMF : 35,35 ; 30,56 y
162,20 ppm.

C₆D₆ : 129,18 ; 127,99 y
126,73 ppm.

MOX : 13,25 ; 54,86 y
67,25 ppm.

ANF : 125,57 ; 131,62 y
136,40 ; 163,37 y
164,31 ppm.

CH₃COOH : 20,67 y 172,62 ppm.

Spectrum "b" shows the chemical shifts of carbons from the monomer mixture (concentrate solution). Spectrum "d" shows the shifts corresponding to the carbons of the copolymer obtained according to the conditions given in Table IV. The total disappearance of the MOX methylene and methyl carbon signals was taken as evidence of the end of the reaction; whereas in the aromatic region, in addition to the copolymer carbon peaks are those of ANF. This was in agreement with the composition found for the copolymers (see Table III). It is also observed that MOX methyl carbon at $\delta = 13,25$ ppm disappears and instead of this, we can see the absorptions at 22,45 and 21.00 ppm which could be assigned to the -COCH₃ methyl carbons. In Spectrum "d" although the absorption of acetic acid C=O carbon was not observed, the peak at $\delta = 21.00$ ppm could also be attributed to the CH₃COOH methyl carbon. To clarify this duality, CH₃COOH was added to the NMR tube in experiment 7,

FIGURE 2. ¹³C-NMR Spectra (C₆D₆, 36°C, 20 MHz)

Spectrum "a": DMF, MOX and C₆D₆.

Spectrum "b": DMF, MOX, C₆D₆ and DMF.

Spectrum "c": DMF, MOX, C₆D₆, ANF and CH₃COOH.

Spectrum "d": Experiment 7, Copolymer MOX/ANF, 330 hours to 60°C.

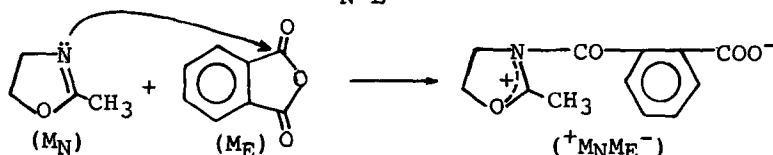
Spectrum "e": Copolymer obtained in experiment 7 and CH₃COOH (after of 30 hours).

(see Spectrum "e") and it was proved that the absorption of methyl carbon of this acid occurs at the same chemical shift as in the case of Spectrum "c", e.i., at $\delta = 20,67$ ppm.

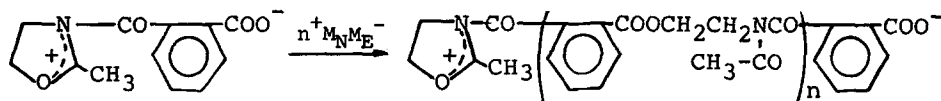
Through experiments performed in bulk, CH_3CN and directly in a ^{13}C -NMR tube it can be concluded that the copolymer partial hydrolysis does not take place during the copolymerization but during the copolymer precipitation and centrifugation, due to the hygroscopic nature of the latter. It is known that the imidic functions are more easily hydrolyzed than the amidic ones; therefore, the copolymer hydrolysis takes place in the $\text{CH}_3\text{CO-N=}$ or the $=\text{N-CO-C}_6\text{H}_4-$ group of the imidic functions. As a result, short chain polymers and CH_3COOH were produced (see in Table II η_{sp}/c).

Copolymerization Mechanism.

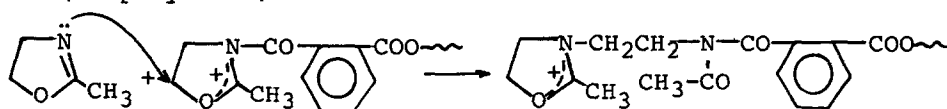
By interaction of MOX (M_N) and ANF (M_E) the genetic zwitterion is formed ($^+M_NM_E^-$):



The propagation may proceed by the reaction of zwitterion with itself (or with the polymeric zwitterion):



or by preferential attack of the pair of electrons of MOX nitrogen on C-5 of the oxazoline ring of the genetic zwitterion (or polymeric).



The fact that copolymers rich in MOX were obtained can be explained if we assume that this last reaction is favorable.

ACKNOWLEDGEMENTS

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