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Spontaneous Copolymerization via Zwitterion

1. 2-Methyl-2-Oxazoline and Succinic Anhydride

B.L. Rivas, G.S. Canessa and S.A. Pooley

Polímeros, Departamento de Química, Facultad de Ciencias, Casilla 3-C,
Universidad de Concepción, Concepción, Chile

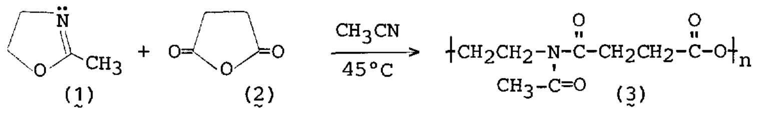
SUMMARY

The copolymers obtained by the spontaneous reaction between 2-methyl-oxazoline (M_N) and succinic anhydride (M_E) are analyzed. The copolymerization takes place at 45^{o}C in CH_3CN without added initiator. The composition of the copolymer was determined by ^{1}H-NMR and ^{13}C-NMR. The scheme of the copolymerization was presented. The genetic zwitterion is not the only species responsible for the propagation as it is deduced from the composition of the copolymers obtained, although its participation in the propagation is important.

INTRODUCTION

In the course of studies on spontaneous copolymerization cyclic imino ethers, nucleophilic monomers reagents (M_N) toward electrophilic-ones (M_E) such as β-propiolactone (Saegusa et al. 1972), methacrilic acid (Balakrishnan et al. 1980), ethylenesulfonamide (Saegusa et al. 1976), acrilic acid (Saegusa et al. 1977) have been used. The interaction between M_N and M_E induced the copolymerizations without adding initiator to give in most cases alternating copolymers via zwitterion intermediates $^{+}M_NM_E^{-}$ (review, Saegusa 1975).

The present paper reports the copolymerization of 2-methyl-2-oxazoline (1) as nucleophilic monomer and succinic anhydride (2) as electrophilic monomer to alternating copolymer:



$$-\!\!\left[CH_2CH_2\text{-}\underset{\substack{| \\ CH_3\text{-}C=O}}{N}\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_2CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\right]\!\!-_n$$

EXPERIMENTAL

<u>Materials</u>. Acetonitrile was purified by distillation over P_2O_5. Succinic anhydride (SAN) was purified by recrystallization from chloroform. 2-Methyl-2-oxazoline (MOX) (Aldrich Chem. Co) was purified by distillation under nitrogen.

<u>Copolymerization</u>. In a glass tube, a mixture of MOX and SAN (0.04 mole total) was dissolved in 10 ml of CH_3CN

under $N_2(g)$. Then the tube was kept at 45°C for 168 h. The copolymerization system was homogeneous during the all reaction. The reaction mixture was poured into 200 ml of diethylether to precipitate a polymeric material. This material was purified by reprecipitation was purified and then dried in vacuo to give a brown gummy hygroscopic material. In the experiment 4 a considerable amount of a white solid (succinic acid) after the solubilization and precipitation of the polymeric material was obtained. The polymer was purified by repeated precipitations.

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

The viscosity of the copolymers was determined by a Ostwald viscometer thermostated at 30.0 ± 0.1°C using DMF as solvent.

RESULTS AND DISCUSSION

The copolymerizations were performed by changing the composition of the comonomers but keeping constant the total mole number (0.04).

The IR spectra of the copolymers show, among others, an absorption band at 1735 cm^{-1} corresponding to the νC=O of the ester group that comes from the opening of the succinic ring; and a band at 1670 cm^{-1} corresponding to the νC=O of the amide coming from the oxazoline ring.

The yields of the copolymerizations and the reduced viscosities increased to reach a maximum value at a initial molar composition of 50/50 (Table I).

Figure 1 shows the ^{1}H-NMR spectra of the copolymers MOX/SAN synthesized from monomeric mixtures with increasing amount of succinic anhydride.

The composition of copolymers was determined by comparison of the integrated values for the methylic hydrogens (3H) centered at $\delta = 2.10$ ppm corresponding to the methyloxazoline present in the copolymer, and the integrated values for the methylenic hydrogens (4H) centered at $\delta = 2.90$ ppm corresponding to the succinic anhydride (Table I).

The same results are obtained when the areas of the methylenic hydrogen of methyloxazoline and succinic anhydride present in the polymeric chain are compared.

Table I shows that the polymers obtained are not identical because there is a preferential incorporation of methyloxazoline in the copolymer obtained.

A brief analysis of the spectra shown in Figure 1 shows that when the ratio of oxazoline incorporated in the copolymers decreases, the intensity of the absorption centered at 3.69 ppm diminishes to reach an intensity very similar to the signal at $\delta = 4.33$ ppm.

The signal centered at $\delta = 3.92$ ppm almost disappears in the spectrum **c** .

The assignment of the signals for the different

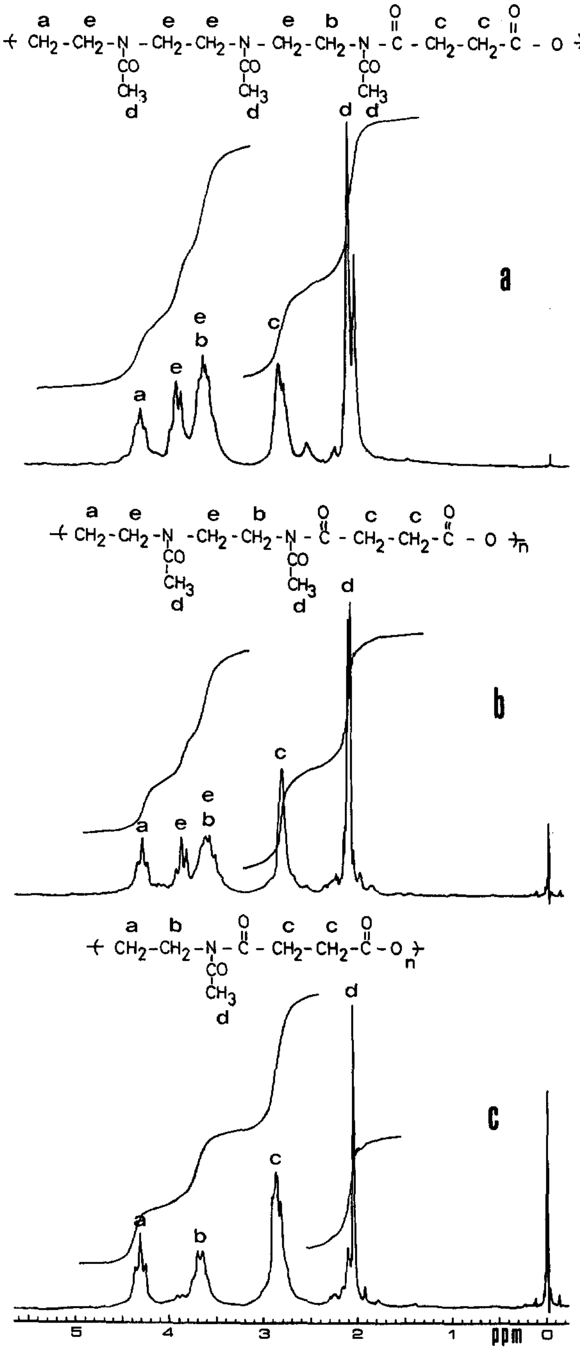


Figure 1. ^{1}H-NMR of copolymers MOX/SAN. (Pyridine-d$_5$; room temp.; TMS).

TABLE I: Copolymerization of 2-Methyl-2-oxazoline (M_N) with Succinic Anhydride (M_E)

Copolymerization Nº	MOX/SAN feed*)	Composition copolymer MOX/SAN by ^{1}H-NMR	Ratio MOX/SAN in Copolymer	Yield %	$\frac{\eta_{sp}}{c}$ †)
1	90/10	71,2/28,8	2,91:1	28,2	0,09
2	70/30	62,2/36,8	2,02:1	58,4	0,10
3	50/50	47,3/52,7	1,06:1	84,7	0,13
4	25/75	63,0/37,0	1,94:1	23,0	$0,12_8$

*) MOX + SAN = 0.04 mole in 10,0 ml of CH_3CN.

†) The measurements were performed in N,N-dimethylformamide at 30°C and a concentration of 0.25 g/100 ml.

type of magnetically non-equivalent hydrogens for each proposed structure, based on the absorption in the corresponding spectra, are shown in Figure 1.

The spectrum **b** corresponds to the copolymer MOX/SAN=2.02:1. The triplet at low field (δ = 4.33 ppm) corresponds to the methylene protons (2H) of $-OCH_2-$ and the multiplet (δ = 3.69 ppm) to imide methylene protons (2H) marked as "b". This signal should be identical in intensity with the 4.33 ppm signal because of the same number of protons involved; nevertheless the signal is twice more intense.

This phenomenon can be explained if half of the 4 inner methylene protons ("e") of the homodiad, that come from the joined methyloxazoline, show a chemical shift at δ = 3.92 ppm and, the other half, that are magnetically non equivalent, absorbs at a different region (3.50 - 3.80 ppm). This region, accidentally corresponds to the absorption area for the "b" protons.

By comparison of the area for the signals of the methylenic hydrogens in the region that goes from 4.5 ppm to 3.5 ppm originated from the polymeric methyloxazoline, it is possible to determine the ratio between them, that is, from low field to high field, of 2:2:4; this data confirms that the structure of the copolymer MOX/SAN is essencially 2:1.

TABLE II: Elemental Analyses of Copolymers

Copolymer Nº	found %		
	C	H	N
1[a]	47,21	7,30	9,50
2[b]	48,20	7,60	9,32
3[c]	47,52	6,10	6,23

[a] Calcd. for $(C_{16}H_{25}N_3O_6)_n$; C, 54.08; H, 7.08; N, 11.83; it is very hygroscopic.

[b] Calcd. for $(C_{12}H_{18}N_2O_5)_n$; C, 53.30; H, 6.66; N, 10.37.
Calcd. for $|C_{12}H_{18}N_2O_5(H_2O)_{1.50}|_n$; C, 48.48; H, 7.07; N, 9.43

[c] Calcd. for $(C_8H_{11}NO_4)_n$ C, 51.89; H, 5.94; N, 7.56.
Calcd. for $|C_8H_{11}NO_4(H_2O)_{1.00}|_n$; C, 47.29; H, 6.40; N, 6.90

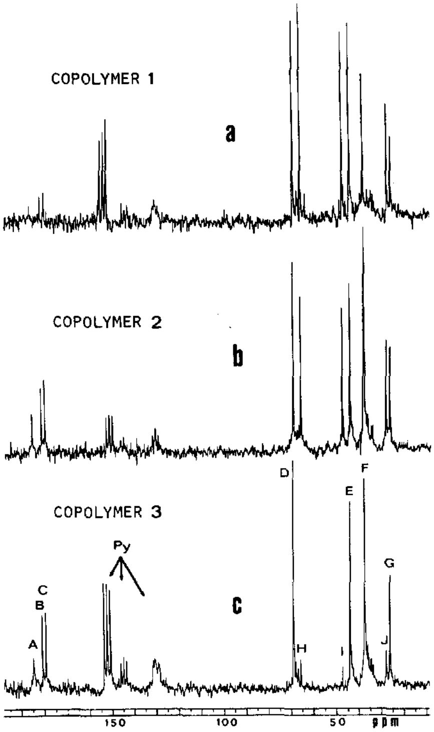


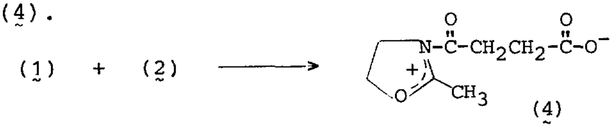
Figure 2. ^{13}C-NMR of copolymers MOX/SAN (C_5D_5N/D_2O; 36°C; 20 MHz).

The spectrum **c** is simpler due to a decrease in the absorption of the homo - diads ("e" protons). From the integration of the protons in the methylenic region (4.5-3.33 ppm) of the methyloxazoline, a value of a 6% of homodiads present in the copolymer was determined, this value agrees with the copolymer composition (1.06:1).
The spectrum **a** in Fig. 1 corresponds to a copolymer methyloxazoline rich (MOX/SAN ratio = 2.91:1). This is confirmed by the strong intensity showed by the signal of the inner protons of the homodiads and homotriads ("e" protons) present in the copolymer.
The copolymerization performed at an initial monomer ratio high in succinic anhydride (MOX/SAN=25/72), produced a copolymer MOX/SAN with a composition close to 2:1 at low yield. A big amount of succinic acid was separated. This acid was characterized by its physical and spectroscopic properties.

The structure of these copolymers was confirmed by ^{13}C-NMR spectroscopy (Fig. 2). The ^{13}C-NMR uncoupled spectrum of copolymer 3(MOX/SAN=1.06:1) show three signals for the carbonyl carbons (A,B,C) at low field; three signals corresponding to the methylene carbons (D,E,F) and one signal for the methyl carbon (G) at high field. Besides, it is possible to recognize the presence of the signals of the homodiads of the methylene and methyl carbons (H,I and J) that are in lower proportion in this copolymer. As it is predicted, these signals are more intense in the spectra of the copolymers MOX rich (spectra **a** and **b**).

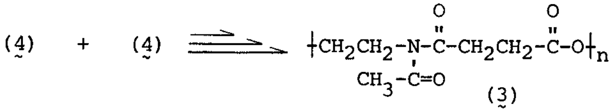
Mechanism of copolymerization

The interaction of 2-methyl-oxazoline (M_N) with succinic anhydride (M_E) produces a genetic zwitterion $^{+}M_NM_E^{-}$ (4).



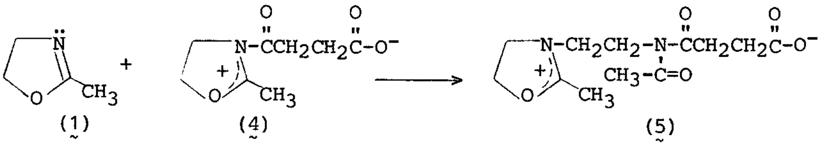
(4)

With an initial equimolar composition of comonomers, the copolymer obtained is essencially alternating. (1.06:1). In this case, the genetic zwitterion is responsible for both, the initiation and propagation steps.

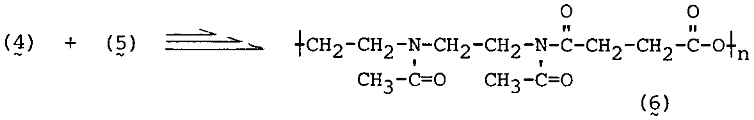


$$(4) + (4) \rightleftharpoons \left[CH_2CH_2-\underset{CH_3-C=O}{N}-\overset{O}{\overset{\|}{C}}-CH_2CH_2-\overset{O}{\overset{\|}{C}}-O \right]_n \qquad (3)$$

From the composition of the copolymers obtained (copolymers 1,2 and 4) it is assumed that the genetic zwitterion is not the only species responsible for propagation. In these cases, the nucleophilic monomer, MOX, must have the possibility of homopropagation. In solution, methyloxazoline would attack the C-5 (electron-defficient center) producing an opening of the oxazolinic ring, generating a zwitterion that contains the MOX homodiads (5).



The anionic part of the other zwitterion (4) attacks the C-5 of the oxazoline ring of the zwitterion (5):



$$(4) + (5) \rightleftharpoons \left[CH_2-CH_2-\underset{CH_3-C=O}{N}-CH_2-CH_2-\underset{CH_3-C=O}{N}-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O \right]_n \qquad (6)$$

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