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Spontaneous copolymerization of 2-phenyl-2-oxazoline with cyclic carboxylic anhydrides

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Summary

The copolymers obtained by the spontaneous reaction between 2-phenyl-2-oxazoline (PhOx) and different anhydrides (succinic - SA, maleic - MA and phthalic - PA) in the absence of an added initiator have been studied. The copolymers were characterized by FTIR and ^{13}C-NMR spectroscopies. Compositions were determined by quantitative elemental analysis and average molecular weights were obtained by GPC. The PhOx/MA and PhOx/PA were found to be alternating copolymers, whereas the PhOx/SA copolymer was a statistical one, rich in PhOx.

Introduction

Usually, polymerization and copolymerization reactions require initiator, catalyst or high-energy radiation. However, there are copolymerizations with occur without initiators. In these cases, an ionic initiating species (zwitterion) is generated by the interaction of a nucleophilic monomer (M_N) with an eletrophilic comonomer (M_E). This type of copolymerization is sometimes called "no-catalyst alternating copolymerization via zwitterion intermediates" or "spontaneous alternating copolymerization via zwitterion intermediates" (1).

$$M_N + M_E \longrightarrow {}^{+}M_N\text{-}M_E$$

$${}^{+}M_N\text{-}M_E + {}^{+}M_N\text{-}M_E^{-} \longrightarrow {}^{+}M_N\text{-}M_E\text{-}M_N\text{-}M_E^{-}$$

$${}^{+}M_N\text{-}M_E\text{-}M_N\text{-}M_E^{-} + {}^{+}M_N\text{-}M_E^{-} \longrightarrow {}^{+}M_N\text{-}(M_E\text{-}M_N)_2\text{-}M_E^{-}$$

$${}^{+}M_N\text{-}(M_E\text{-}M_N)_m\text{-}M_E^{-} + n\,{}^{+}M_N\text{-}M_E^{-} \longrightarrow {}^{+}M_N\text{-}(M_E\text{-}M_N)_{m+n}\text{-}M_E^{-}$$

Saegusa et al. carried out a series of studies on spontaneous copolymerizations between cyclic imino ethers (M_N) and several eletrophilic monomers (M_E) (2 - 6).

In recent years, spontaneous copolymerizations of 2-methyl-2-oxazoline (7 - 9) or 2-ethyl-2-oxazoline (10 - 12) with cyclic carboxylic anhydrides have been reported by Rivas et al.

In the present paper is reported the synthesis of spontaneous alternating copolymers via zwitterion by reacting 2-phenyl-2-oxazoline with cyclic carboxylic anhydrides.

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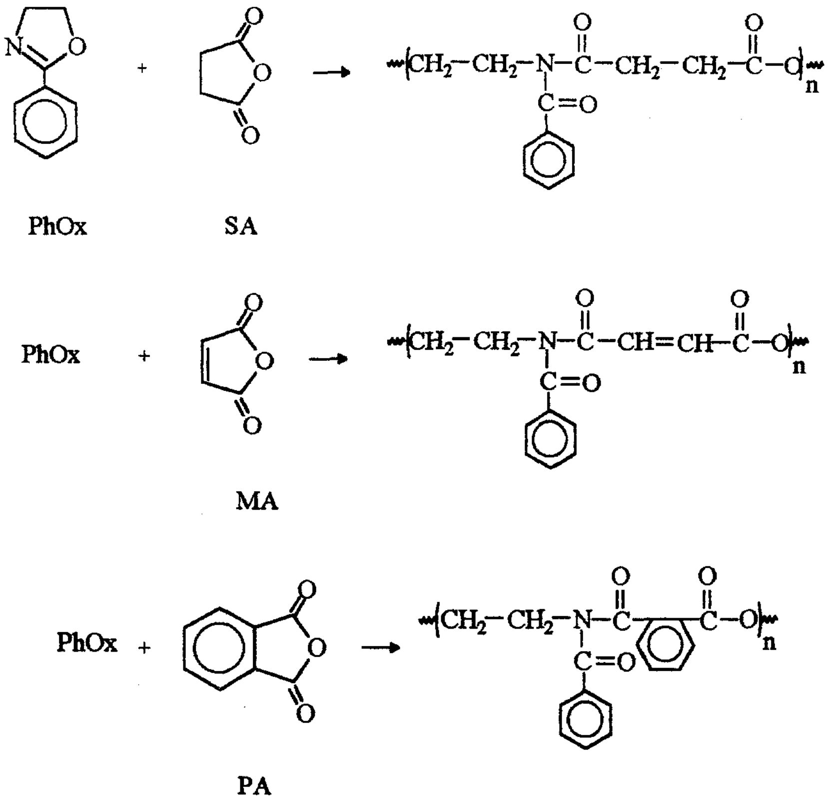
Figure 1 - Copolymer synthesis



Experimental

Materials: 2-Phenyl-2-oxazoline was synthesised and purified according to the literature (13, 14). Succinic anhydride (BDH) was purified by recrystalization from chloroform. Maleic (BDH) and phthalic anhydride (Herzog) were purified by triple resublimation. Acetonitrile (Riedel), N,N-dimethyl-formamide (DMF) (Reagen), chloroform (Vetec) and ethyl ether (Vetec) were twice distilled. Other reagents and solvents were purified when needed by usual methods.

Copolymerizations: In glass tubes, the monomer mixtures were dissolved in 15 ml of solvent and the systems were kept under N_2, at a select temperature for 360 h (Table 1). After this time, the reaction mixtures were poured into 250 ml of ethyl ether to precipitate the polymeric material, separated by filtration, purified by sucessive dissolutions and precipitations, and dried under vacuum.

Measurements: FTIR spectra were recorded on a Perkin-Elmer 1720 X. The ^{13}C-NMR spectra were recorded on a Varian Gemini VXR-300. The elemental analyses were carried out on a Perkin-Elmer 240 C. The average molecular weights were determined on a Waters

600 E gel permeation chromatograph equipped with RI (Waters 410) and photodiode detector (Waters 991) (standard: polystyrene; Waters Ultrastyragel columns of 500 Å, 10^3 Å, 10^4 Å and 10^5 Å). The viscosity of copolymers was determined in a Ubbelohde viscosimeter thermostated at 25°C ± 0.1°C using DMF as solvent.

Results and discussion

The copolymerization reactions between 2-phenyl-2-oxazoline (PhOx), as nucleophilic monomer and succinic anhydride (SA), maleic anhydride (MA) and phtalic anhydride (PA), as eletrophilic monomers, were carried out keeping constant the total mole number (0.07). The Table 1 shows the copolymerization conditions.

Table 1 - Polymerization conditions

Copolymer	PhOx/CCA* initial ratio (%)	Solvent	Temperature (°C)	Yield (%)
PhOx/SA	50/50	CH_3CN	55	17.32
PhOx/MA	50/50	CH_3CN	55	56.98
PhOx/PA	50/50	DMF	85	62.55

*CCA - cyclic carboxylic anhydrides

The copolymers PhOx/MA and PhOx/PA are black and white hygroscopic solids, respectively, and are soluble in acetone, 1,4-dioxane, THF, DMF, ethanol, methanol and chloroform. The copolymer PhOx/SA is a white hygroscopic solid soluble in DMF and chloroform.

The FTIR spectra of the copolymers are similar. They did not show the characteristic frequency of anhydride carbonyl and showed, among others, characteristic absorption bands of the ester and amide carbonyl at 1720 cm^{-1} and 1640 cm^{-1} respectively, which confirms the opening of cyclic anhydrides and oxazoline rings (Figure 2).

Figure 3 shows the ^{13}C-NMR spectra of the copolymers PhOx/MA and PhOx/SA prepared in the solid state, and of the copolymer PhOx/PA determined in $CDCl_3$ solution. The ^{13}C-NMR spectra showed signals in the range of 167.8 - 172.6 ppm (amide carbonyl), 174.6 - 182.9 ppm (ester carbonyl), 122.3 - 133.6 ppm (aromatic ring) and 28.4 - 38.6 (metylene carbons) for the three copolymers.

The compositions of the copolymers were determined by quantitative elemental analysis (Tables 2 and 3). The N/C ratio was used to calculate copolymer composition because it is unaffected by the water occluded in the copolymers; these values are in good agreement with the calculated values for the different copolymers.

Table 2 - Elemental analysis of the copolymers

Copolymer	C (%)	H (%)	N (%)
Exp. PhOx/SA	62.8	6.6	6.4
Calc. $(PhOx)_{1.0}/(SA)_{0.75}/(H_2O)_{0.4}$	62.8	5.6	6.1
Exp. PhOx/MA	62.3	5.6	5.4
Calc. $(PhOx)_{1.0}/(MA)_{1.0}/(H_2O)_{0.3}$	62.2	4.6	5.6
Exp. PhOx/PA	63.3	5.4	4.4
Calc. $(PhOx)_{1.0}/(PA)_{1.0}/(H_2O)_{1.5}$	63.4	5.0	4.4

Table 3 - Copolymer compositions

Copolymer	Monomer ratio	Copolymer* composition	N/C (theor.)	N/C* (exp.)
PhOx/SA	1.0 : 1.0	1.0 : 0.75	0.0971	0.1019
PhOx/MA	1.0 : 1.0	1.0 : 1.0	0.0900	0.0867
PhOx/PA	1.0 : 1.0	1.0 : 1.0	0.0694	0.0695

* Determined bythe elemental analysis

The PhOx/MA and PhOx/PA compositions of the products obtained by elemental analysis confirmed the alternating character of these copolymers. It was found that the PhOx/SA composition is statistical, and it showed that the proportion of PhOx in the copolymer is higher than that of SA.

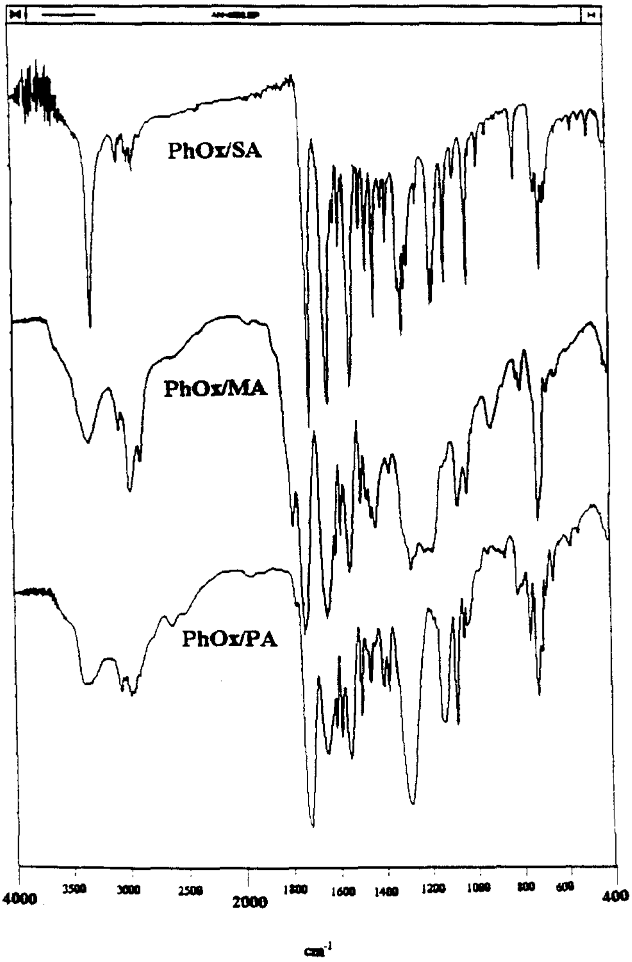


Figure 2 - FTIR spectra of copolymers.

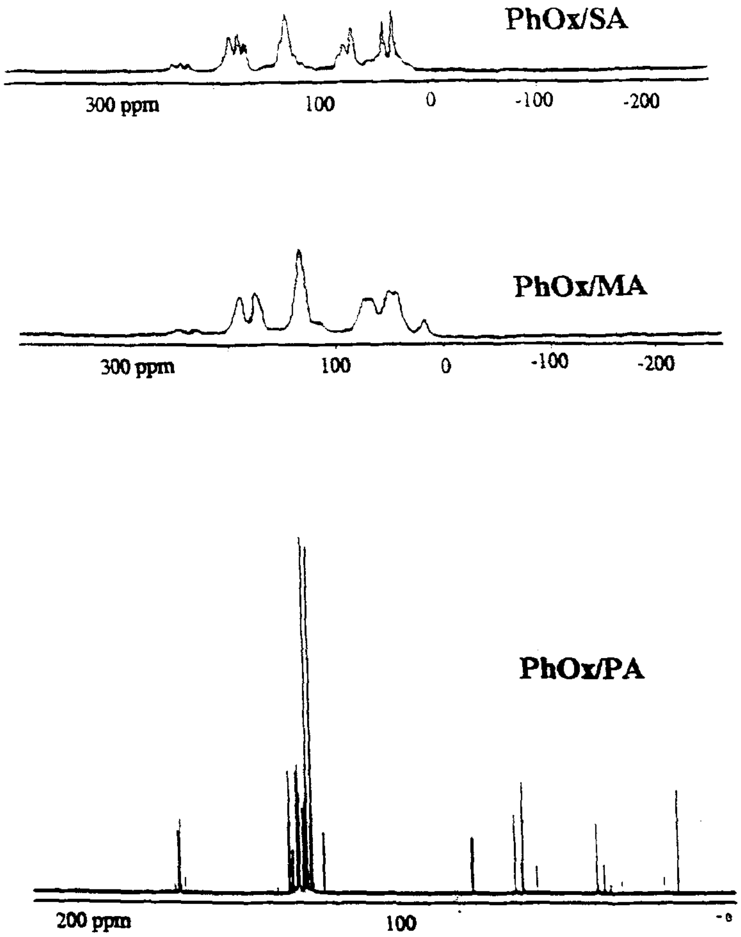


Figure 3 - ^{13}C-NMR spectra of copolymers

The relative viscosities were measured in DMF at 25°C and the average molecular weights were obtained by GPC using THF as solvent (Table 4).

Table 4 - GPC* and viscosity results

Copolymer	M_n	M_w	M_w/M_n	η_{sp}/C** (dl/g)
PhOx/SA	991	1382	1.4	0.0510
PhOx/MA	11804	17141	1.5	0.1302
PhOx/PA	818	1116	1.4	0.0406

*in THF / **in DMF at 25°C (0.5 g/dl)

The PhOx/MA showed higher relative viscosity (0.5 dl/g) than the other copolymers, that it was confirmed by the average molecular weight determined by GPC.

The copolymerizations mechanisms are analogous to those proposed for other copolymerizations (7 - 9).

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