

Copolymerization via zwitterion

11. N-Phenylmaleimide with 2-ethyl-2-oxazoline

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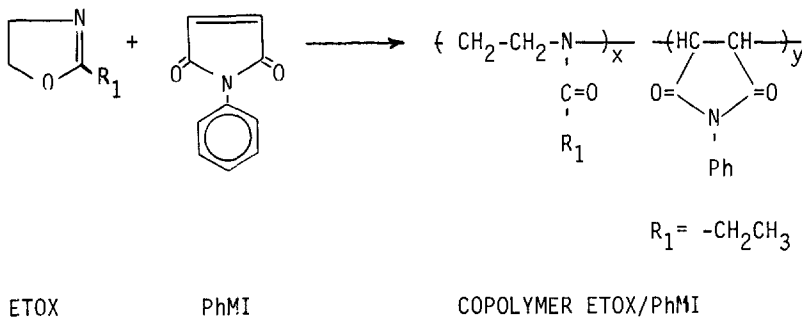
SUMMARY

Copolymers of 2-ethyl-2-oxazoline (ETOX) and N-phenylmaleimide (PhMI) without initiator were prepared at different feed mole ratios, solvents, temperatures and times. The copolymers are almost statistical and rich in N-phenylmaleimide. The copolymer composition was determined by ¹H NMR.

INTRODUCTION

Zwitterion copolymerization occurs in the absence of an added initiator by reacting an electrophilic monomer (ME) and a nucleophilic monomer (MN) (1-10). This copolymerization is considered to proceed through zwitterion intermediates ⁺MNME⁻ leading to alternating or statistical copolymers. Among the nucleophilic or electrophilic monomers studied by other authors or by us are: cyclic iminoethers, ethyleneimine, cyclic phosphites, α,β-unsaturated acids, lactones, sultones, cyclic anhydrides, N-phenylmaleimide (1-10).

The present paper reports the copolymerization of 2-ethyl-2-oxazoline nucleophilic monomer with N-phenylmaleimide as the electrophilic monomer. The copolymerization was carried out under different experimental conditions (feed mole ratio, temperature, time and solvent).



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EXPERIMENTAL PART

Materials: N-phenylmaleimide (PhMI) was synthesized according to the literature(11). 2-Ethyl-2-oxazoline (ETOX) (commercial reagent Aldrich Chem. Co.) was purified by distillation from KOH. All the solvents were purified by usual methods (12).

Copolymerization: An example is as follows: In a polymerization flask, a mixture of ETOX (0.06 mole) and PhMI (0.06 mole) under gaseous N_2 was dissolved in the solvent. Then the system was kept at 60°C for 90 h. The copolymerization mixture was poured in 250 ml of diethyl ether giving a pinkish-white polymeric material. It was purified by reprecipitation and dried under vacuum.

Measurements: 1H NMR spectra were recorded at room temperature on a Varian T 60 A using in $CDCl_3$ solutions with TMS as internal standard. The IR spectra were recorded on a Perkin Elmer 577 spectrophotometer. The viscosity of the copolymer was determined using DMF solvent and an Ostwald viscometer, at $30.0 \pm 0.1^\circ C$.

RESULTS AND DISCUSSION

In the last few years we have reported several copolymerization systems, one of them being the phthalic anhydride with 2-methyl-2-oxazoline statistical copolymers rich in the nucleophilic monomer (13). Simionescu and co-workers (5) have reported the copolymerization of N-phenylmaleimide with 2-methyl-2-oxazoline. We now report the copolymerization of N-phenylmaleimide (PhMI) with 2-ethyl-2-oxazoline (ETOX).

Copolymerizations were carried out at different feed mole ratios but keeping the total amount of comonomers constant (See Table 1). The copolymerization conditions are summarized in the Table 1.

The PhMI/ETOX copolymers are pinkish-white, soluble in organic solvents such as $CHCl_3$, DMSO, pyridine.

The highest conversion, determined from the insoluble fraction in diethyl ether, was obtained with a feed mole ratio of ME:MM (2:1)(Table 1, copolymers 3,6,10) With increasing time the yield increases. (See Table 1, copolymers 1,4 and 7). For copolymer 7 (90h, 60°C) the yield is 79.7%. Temperature increases conversions. The intrinsic viscosity of the copolymers increases with increasing temperature (See Table 1, copolymers 7, 8 and 9).

The effect of solvent polarity on the yield and the copolymer viscosity were studied assuming that the copolymerization occurs via dipole ionic species. The highest yield is obtained in the most polar solvent, CH_3CN . However, the highest intrinsic viscosity is obtained in an apolar solvent, benzene (See Table 2).

Table 1.- Conditions and results of the solution copolymerization of 2-ethyl-2-oxazoline (ETOX) with N-phenylmaleimide (PhMI) at different temperatures and times of copolymerization.

Copolymer	ETOX (mole)	PhMI (mole)	Time (h)	Temp. (°C)	Yield (%)	[η] dl/g	N/C* ratio	Copolymer Composition	
								from N/C ratio	from $^1\text{H NMR}$
1	0.006	0.006	24	60	28.2	0.089	0.1248	7.0 : 1.0	7.4 : 1.0
2	0.008	0.004	24	60	24.7	0.078	0.1286	4.3 : 1.0	4.3 : 1.0
3	0.004	0.008	24	60	45.7	0.096	0.1226	9.4 : 1.0	9.5 : 1.0
4	0.015	0.015	42	60	44.6	0.067	0.1370	2.4 : 1.0	2.5 : 1.0
5	0.020	0.010	42	60	17.0	0.058	0.1306	4.4 : 1.0	4.4 : 1.0
6	0.010	0.020	42	60	71.9	0.072	0.1304	3.7 : 1.0	3.8 : 1.0
7	0.015	0.015	90	50	66.3	0.038	0.1358	2.5 : 1.0	2.5 : 1.0
8	0.006	0.006	90	60	79.7	0.046	0.1400	2.0 : 1.0	2.0 : 1.0
9	0.015	0.015	90	70	85.0	0.092	0.1635	1.0 : 1.0	1.1 : 1.0
10	0.010	0.020	90	70	90.2	0.111	0.1395	4.0 : 1.0	4.2 : 1.0
11	0.020	0.010	90	70	45.0	0.089	0.1442	1.6 : 1.0	1.9 : 1.0

*) obtained from elemental analyses.

The IR spectra of the copolymers show absorption bands at 1700 cm^{-1} , corresponding to $\nu_{\text{C}=\text{O}}$ (anhydride), and at 1625 cm^{-1} corresponding to $\nu_{\text{C}=\text{O}}$ (amide) due to the opening of the oxazoline ring (See Fig. 1).

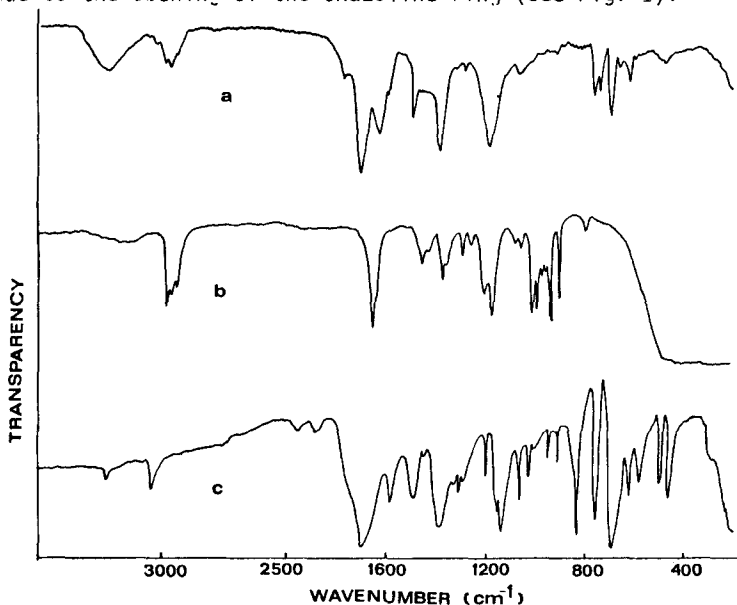


Figure 1. IR spectra of a) Copolymer 9 PhMI/ETCX
b) 2-Ethyl-2-oxazoline and c) Phenylmaleimide

^1H NMR spectra of the copolymers (Figure 2) show four signals assigned as follows: signal (a) at $\delta=0.9-1.4$ to CH_3 protons, signal (b) at $\delta=2.1-2.6$ to $-\text{CH}_2\text{CH}_3$ protons; signal (c) at $\delta=3.0-4.2$ ($-\text{CH}$ and $-\text{CH}_2\text{CH}_2\text{N}-$) protons, and signal (d) at $\delta=7.0-7.7$ to aromatic protons.

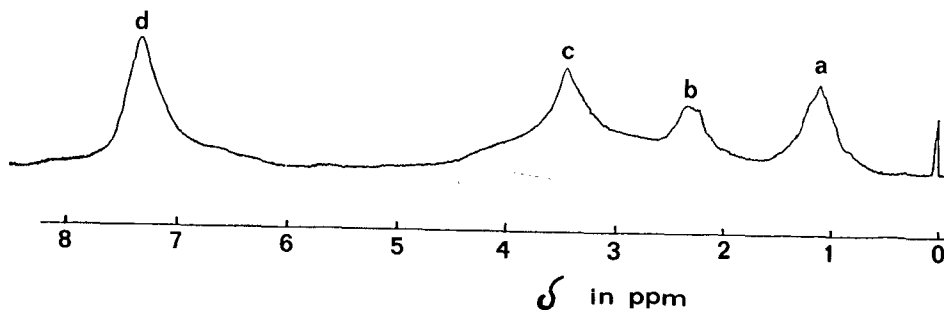


Figure 2. ^1H NMR spectrum (60 MHz, CDCl_3 , TMS, room temperature) of Copolymer 9 PhMI/ETOX.

Table 2.- Effect of solvent polarity(d_{40}^20 ,const. ϵ) on the yield, intrinsic viscosity and copolymer composition. Polymerization were carried with a 1:1 monomer mole ratio in the charge at 70°C, 90h.

Copolymer	EtOX (mole)	PhMI (mole)	Solvent (5ml)	ϵ	Yield (%)	[η] dl/g	N/C ^a ratio ^a	Copolymer Composition	
								from N/C ratio	from ¹ H NMR
12	0.015	0.015	CH ₃ CN	37.5	84.9	0.092	0.1635	1.0 : 1.0	1.1 : 1.0
13	0.010	0.010	CH ₃ COCH ₂ CH ₃	18.5	25.2	0.133	0.1396	2.0 : 1.0	1.9 : 1.0
14	0.015	0.015	C ₆ H ₆	2.3	25.0	0.150	0.137E	2.3 : 1.0	2.2 : 1.0

^a) determined from elemental analyses.

The copolymer composition was determined by comparing the equivalent area of protons in the ME and MN units incorporated into the copolymer (see Table 1). The proton area of the MN unit was determined from the methyl protons which resonate between $\delta=0.9$ and 1.4 and for ME it was determined from the aromatic protons which resonate between $\delta=7.0$ and 7.7.

Copolymer compositions determined by ^1H NMR are very similar to that determined from the elemental analyses, using the ratio N/C, (this ratio is independent of the occluded water in the copolymer).

Almost all the copolymers are statistical and rich in the electrophilic unit.

By increasing the dielectric constant of the solvent, temperature, and copolymerization time, decreases the extent of incorporation of electrophilic unit approaching the alternating copolymer. In the case of copolymer 9 (90h, 70°C) alternating copolymer is obtained (See Table 1). Similarly, alternating copolymer arises in the presence of acetonitrile (See Table 2).

With respect to the copolymerization mechanism, alternating copolymers are formed by the addition of the nucleophilic monomer (ETOX) to the double bond of the electrophilic monomer (PhMI) giving a zwitterion, the responsible species for initiation and propagation. The statistical copolymers which are richer in PhMI, arise by propagation by preferential attack on the double bond of PhMI. In fact, the maleimide polymerizes by anionic initiators (14). Nevertheless it was not possible to detect by ^1H NMR spectroscopy (60 MHz) the other possibility, that is the attack of the nucleophilic monomer on the carboxylic group of the phenylmaleimide giving a copolymer with a double bond in the structure.

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