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Copolymerization via zwitterion of 2-ethyl-2-oxazoline with β-methylhydrogenitaconate

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SUMMARY

2-Ethyl-2-oxazoline (ETOX) as a nucleophilic monomer and β-methylhydrogenitaconate (MHI) as electrophilic monomer were copolymerized in solution in the absence of initiator at various feed mole ratios. Copolymers were characterized by elemental analysis, FT-IR and ^{1}H NMR spectroscopy. The copolymer composition was determined by elemental analysis and by ^{1}H NMR spectroscopy. The copolymerization reaction occurs with a termination reaction which is evidenced by the end double bond at the ^{1}H NMR spectra.

INTRODUCTION

Copolymerization via zwitterion intermediates, in which a nucleophilic monomer (MN) and electrophilic monomer (ME) are combined to produce a zwitterion as the key intermediate (1-10). In these copolymerizations, cyclic iminoethers, such as 2-oxazolines, and aziridine derivates have been used as MN and reacted with the electrophilic monomers such as β-propiolactone, acrylic acid, succinic anhydride, N-phenylmaleimide and derivatives.

Normally, the "genetic zwitterion" $^+$MNME$^-$ **1** is responsible for the initiation as well as for the propagation reaction. The following general scheme shows the growth of the "genetic zwitterion" **1** into oligo- and macrozwitterion.

$$\mathbf{1} + \mathbf{1} \longrightarrow {}^+\text{MNME - MNME}^- \quad \mathbf{2}$$

$$\mathbf{2} + \mathbf{1} \longrightarrow {}^+\text{MN(MEMN)}_2\text{ME}^- \quad \mathbf{3}$$

$${}^+\text{MN(MEMN)}_n\text{ME}^- + \mathbf{1} \longrightarrow {}^+\text{MN(MEMN)}_{n+1}\text{ME}^-$$

The present paper reports the copolymerization of 2-ethyl-2-oxazoline as nucleophilic monomer with β-methylhydrogenitaconate as electrophilic monomer. The copolymerizations were carried out under various experimental conditions (feed mole ratios, temperature, time and solvent).

EXPERIMENTAL

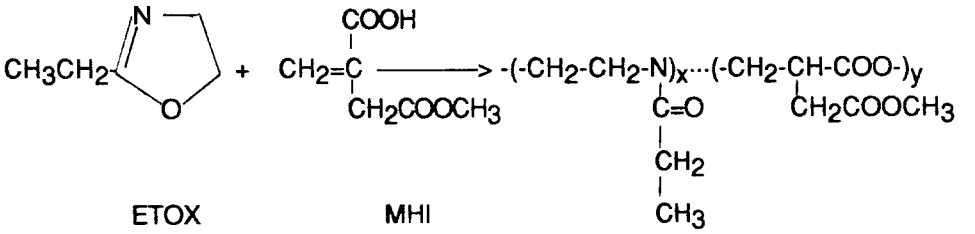
Materials: 2-Ethyl-2-oxazoline (ETOX) (Commercial reagent Aldrich Chemical Co.) was purified by distillation from KOH. β-Methylhydrogenitaconate (MHI) was synthesized and purified according to Baker et al. (11). The solvents were purified by the usual methods (12).

Copolymerization: A typical procedure for the copolymerization is as follows: the mixture of ETOX and MHI (total amount 0.020 mol) was placed in a vessel under N_2. The tube was kept at the desired temperature for several hours. The mixture was poured in diethyl ether giving a polymeric material. The copolymer was separated by centrifugation, purified by reprecipitation and dried in vacuum.

Measurements: The viscosity of the copolymer was determined using DMF as solvent and an Ostwald viscometer at 30.0 ± 0.1°C. The FT-IR and ^1H NMR spectra were recorded on a Bruker IFS-48 spectrophotometer and on a Bruker AC 250 spectrometer respectively. The chemical shifts were reported (in ppm) relative to internal standard.

RESULTS AND DISCUSSION

The copolymerizations of ETOX with MHI in absence of any added initiator were carried out varying the initial composition between both monomers but keeping constant the total amount of comonomers (0.02 mol).



All the poly(2-ethyl-2-oxazoline-**co**-β-methylhydrogenitaconate)s are soluble in $CHCl_3$.

The copolymerization conditions are summarized in Table 1.

For equimolar feed mole ratios ETOX/MHI, the conversion increases with increasing the copolymerization times (copolymer 1 and 6). The same effect is observed with the temperature (copolymer 1, 4-6) producing the highest conversion yield at 70°C (90%), determined from the insoluble fraction in diethyl ether (copolymer 5). The conversions are higher than those observed for poly(2-methyl-2-oxazoline-**co**-β-methylhydrogenitaconate) (10-43%) probably due to a poor reaction between the two monomers to produce the first zwitterion ("genetic zwitterion") or to a slow propagation (13). The more polar solvent acetonitrile produces a copolymer with higher yield and intrinsic viscosity.

Table 1. Results of the solution copolymerization of 2-ethyl-2-oxazoline (ETOX) with β-methylhydrogenitaconate (MHI).

Copolymer Nº	ETOX (mol)	MHI (mol)	Solvent (5 ml)	Time (h)	Temperature (°C)	Yield (%)	[η] ($dl \cdot g^{-1}$)	Copolymer composition ETOX/MHI from	
								Elem. Anal.	^1H NMR
1	0.010	0.010	CH_3CN	48	60	83	0.016	1.0 : 1.1	1.0 : 1.2
2	0.013	0.007	CH_3CN	48	60	80	0.010	1.0 : 1.0	1.0 : 1.1
3	0.007	0.013	CH_3CN	48	60	46	0.018	1.0 : 1.4	1.0 : 1.3
4	0.010	0.010	CH_3CN	48	50	85	0.050	1.0 : 1.0	1.0 : 1.0
5	0.010	0.010	CH_3CN	48	70	90	0.001	1.0 : 1.0	1.0 : 1.1
6	0.010	0.010	CH_3CN	24	60	80	0.001	1.0 : 1.1	1.0 : 1.1
7	0.010	0.010	CH_3CN	64	60	85	0.021	1.0 : 1.0	1.0 : 1.1
8	0.010	0.010	$CH_3CH_2COCH_3$	48	60	75	0.015	1.0 : 1.2	1.0 : 1.3
9	0.010	0.010	C_6H_6	48	60	79	0.011	1.0 : 1.1	1.0 : 1.2

The FT-IR spectra of all the copolymers show similar absorption bands at 1642 cm^{-1} corresponding to $\nu_{C=O}$(amide) and at 1733 cm^{-1} corresponding to $\nu_{C=O}$(esther) which confirm the opening of oxazoline ring and the reaction with the double band of MHI (see figure 1).

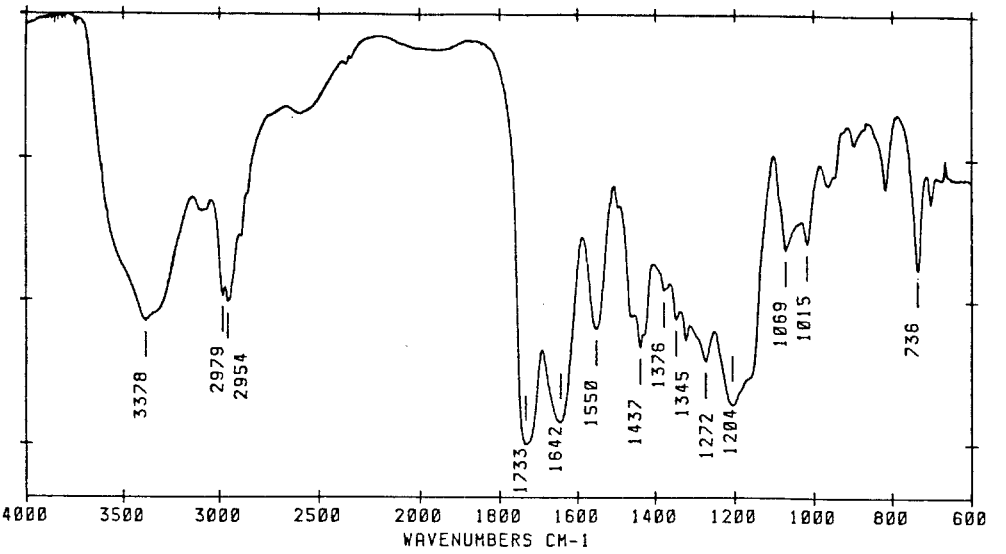


Figure 1. FT-IR spectrum of the poly(2-ethyl-2-oxazoline-**co**-β-methylhydrogenitaconate), sample 1.

The 250 MHz ^1H NMR spectra of the copolymers ETOX/MHI show the following signals (a) at δ = 1.14, CH_3 protons from ETOX; signal (b) at δ = 2.01-2.33, $-CH_2-CH_3$ protons; signal (c) at δ = 2.72, >CH-proton, signal (d) at δ = 3.37-3.75 $-CH_2-N<$ protons; signal (e) at δ = 4.24, OCH_2-; signal (f) at δ = 5.72-6.31 -CH=CH- protons, and signal (g) at δ = 7.37 ppm corresponds to the proton from $CDCl_3$ 99.9% (see Figure 2).

The copolymer composition was determined by comparing the equivalent proton area of the ME and MN units incorporated into the copolymer (see Table 1). In general, the compositions obtained by ^1H NMR spectra are slightly different from those found from the N/C ratio calculated from elemental analysis.

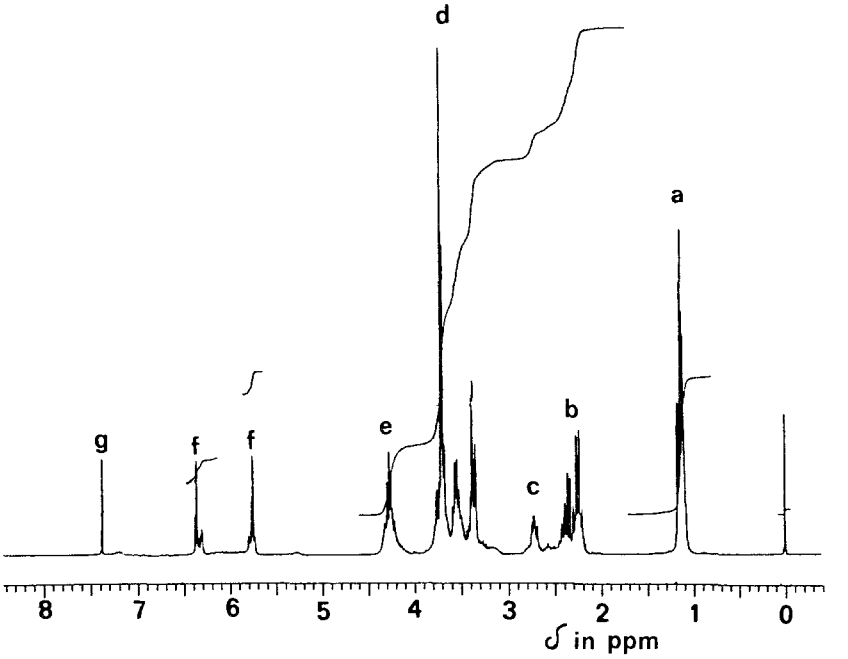


Figure 2. ^1H NMR spectrum (250 MHz, $CDCl_3$, TMS as internal standard of the poly(2-ethyl-2-oxazoline-**co**-β-methylhydrogenitaconate).

The copolymers show alternating tendency; the more polar solvent CH_3CN would favor the interaction between the monomers forming genetic zwitterion and the propagation by these species. However, the homopropagation reaction of the electrophilic monomer MHI is faster using 2-butanone and benzene as well as by an excess of MHI in the feed.

The mechanism is similar to that of 2-methyl-2-oxazoline with β-methylhydrogenitaconate (13), which involves the formation of "genetic zwitterion ion". Growth proceeds by condensation of different sized zwitterions with the genetic zwitterion and also between them to form alternating copolymers. For some copolymerizations, homopropagation of MHI occurs due to ion-dipole reactions between ionic centers of zwitterions and MHI.

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