

Spontaneous copolymerization of 1-(2-hydroxyethyl)aziridine with *N*-phenylmaleimide and *p*-methoxyphenylmaleimide

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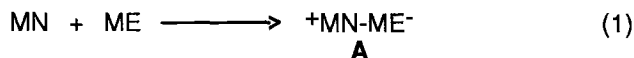
SUMMARY

The copolymerization of 1-(2-hydroxyethyl)aziridine as nucleophilic monomer with *N*-phenylmaleimide and *p*-methoxyphenylmaleimide as electrophilic monomer in the absence of an initiator in solution was investigated. Copolymerizations under different experimental conditions were carried out. The copolymers were characterized by FT-IR and ¹H-NMR spectroscopy. The copolymer compositions were determined by elemental analysis and ¹H-NMR spectroscopy. Almost all products are statistical copolymers.

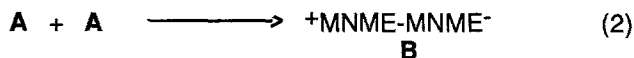
INTRODUCTION

Spontaneous copolymerizations have been reported for nucleophilic monomers, such as cyclic imino ethers with electrophilic monomers, such as lactones (1-4), sulfones (5), α,β-unsaturated acids (6-10), cyclic anhydrides (11-13).

These copolymerizations occur in the absence of an initiator by interaction of an electrophilic monomer (ME) with a nucleophilic monomer (MN) producing a "genetic zwitterion" A.



which is responsible for initiation and propagation:



In general:



Homopropagation between a zwitterion and comonomer was also proposed:



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The latter reactions become important for copolymerization systems leading to statistical copolymers.

This paper reports the copolymerization of 1-(2-hydroxyethyl)aziridine (HEA) as nucleophilic monomer with N-phenylmaleimide (N-PhMI) and p-methoxyphenylmaleimide (p-MeOPhMI) as electrophilic monomer.

EXPERIMENTAL PART

Materials: 1-(2-hydroxyethyl)aziridine (from Aldrich) was purified by distillation under nitrogen. N-phenylmaleimide and p-methoxyphenylmaleimide were synthesized by a published method (14). Solvents were purified by the usual methods (15).

Copolymerization: Copolymerization was carried out. Various HEA and N-PhMI or p-MeOPhMI concentrations were used under N_2 keeping constant the total number of moles. The flasks were placed in a thermostat at constant temperature. The charges were precipitated in diethyl ether. The copolymers were purified by reprecipitation and dried under vacuum to constant weight.

Measurements: FT-IR spectra were recorded on a Bruker IFS-48 spectrophotometer. ^1H NMR spectra were registered at room temperature on a Bruker AC 250 and on a Varian XL-100 spectrometer. The viscosity of the copolymers was determined with an Ostwald viscometer, thermostated at 30.0 ± 0.1 °C using DMF as solvent.

RESULTS AND DISCUSSION

Copolymerizations of HEA with N-PhMI and p-MeOPhMI were carried out at various mole ratios. (see Tables 1 and 2).

The highest copolymerization yields near quantitative were obtained with CH_3CN at 50°C in 24 h.

The yield decreases, by decreasing the dielectric constant of the solvent.

The FT-IR spectra of the copolymers N-PhMI/HEA and p-MeOPhMI/HEA show signals at 1712 cm^{-1} , correspondent to $\nu(\text{C}=\text{O})$ and at 3368 cm^{-1} assignable to $\nu(\text{OH})$. (see Fig. 1).

The ^1H NMR for N-PhMI/HEA copolymers spectra show the following signals: **a** at $\delta=2.48\text{-}2.57$ attributed to $-\text{CH}_2\text{-N-CH}_2-$; **b** at $\delta=2.72\text{-}2.87$ assigned to CH-CH ; **c** at $\delta=3.48$ attributed to $-\text{CH}_2\text{-O-}$ and **d** at $\delta=7.01\text{-}7.43$ ppm assigned to aromatic protons (see Fig. 2).

Table 1. Conditions and results of the solution copolymerization of N-Phenylmaleimide (N-PhMI) with 1-(2-hydroxyethyl) aziridine (HEA)

Copolymer No	N-PhMI (mol)	HEA (mol)	Yield (%)	Temp. (°C)	Time (h)	Solvent (5ml)	N/C ratio	[η] (dl/g)	Copol. Composition		ME:MN
									from Elem. Anal.	from $^1\text{H-NMR}$	
1	0.015	0.015	96.5	50	24	CH ₃ CN	0.1648	0.040	1.0:1.0	1.0:1.0	1.0:1.0
2	0.020	0.010	85.0	50	24	CH ₃ CN	0.1495	0.027	1.7:1.0	1.6:1.0	1.6:1.0
3	0.010	0.020	82.4	50	24	CH ₃ CN	0.2026	0.016	0.4:1.0	1.0:2.3	1.0:2.3
4	0.015	0.015	85.6	50	24	C ₆ H ₆	0.1737	0.029	0.8:1.0	1.0:1.5	1.0:1.5
5	0.015	0.015	79.7	50	24	CH ₃ COCH ₂ CH ₃	0.1710	0.034	0.9:1.0	1.0:1.3	1.0:1.3
6	0.015	0.015	92.0	40	24	CH ₃ CN	0.1664	0.035	1.0:1.0	1.0:1.0	1.0:1.0
7	0.015	0.015	78.3	50	32	CH ₃ CN	0.1818	0.024	0.7:1.0	1.0:1.3	1.0:1.3
8	0.015	0.015	96.3	50	42	CH ₃ CN	0.1759	0.018	0.6:1.0	1.0:1.5	1.0:1.5
9	0.015	0.015	89.9	30	24	CH ₃ CN	0.1853	0.013	0.7:1.0	1.0:1.5	1.0:1.5

Table 2. Conditions and results of copolymerization of p-methoxyphenylmaleimide (p-MeOPhMI) with 1-(2-hydroxyethyl)aziridine (HEA).

N ^o	p-MeOPhMI (mol)	HEA (mol)	Yield (%)	Temp. (°C)	Time (h)	Solvent (5ml)	N/C ratio	Copolymer Composition	
								from Elem. Anal.	ME:MN ¹ H-NMR
1	0.012	0.012	98.2	50	24	CH ₃ CN	0.1279	2.7:1.0	2.7:1.0
2	0.016	0.008	78.2	50	24	CH ₃ CN	0.1220	3.8:1.0	3.9:1.0
3	0.008	0.016	98.5	50	24	CH ₃ CN	0.1463	1.5:1.0	1.5:1.0
4	0.012	0.012	98.9	50	32	CH ₃ CN	0.1250	3.2:1.0	3.3:1.0
5	0.012	0.012	99.0	50	72	CH ₃ CN	0.1268	2.9:1.0	3.0:1.0
6	0.012	0.012	95.8	30	24	CH ₃ CN	0.1364	1.9:1.0	2.1:1.0
7	0.012	0.012	85.3	40	24	CH ₃ CN	0.1281	2.7:1.0	2.7:1.0
8	0.012	0.012	70.1	50	24	C ₆ H ₆	0.1354	1.9:1.0	2.1:1.0
9	0.012	0.012	91.8	50	24	CH ₃ CH ₂ COCH ₃	0.1298	2.5:1.0	2.6:1.0

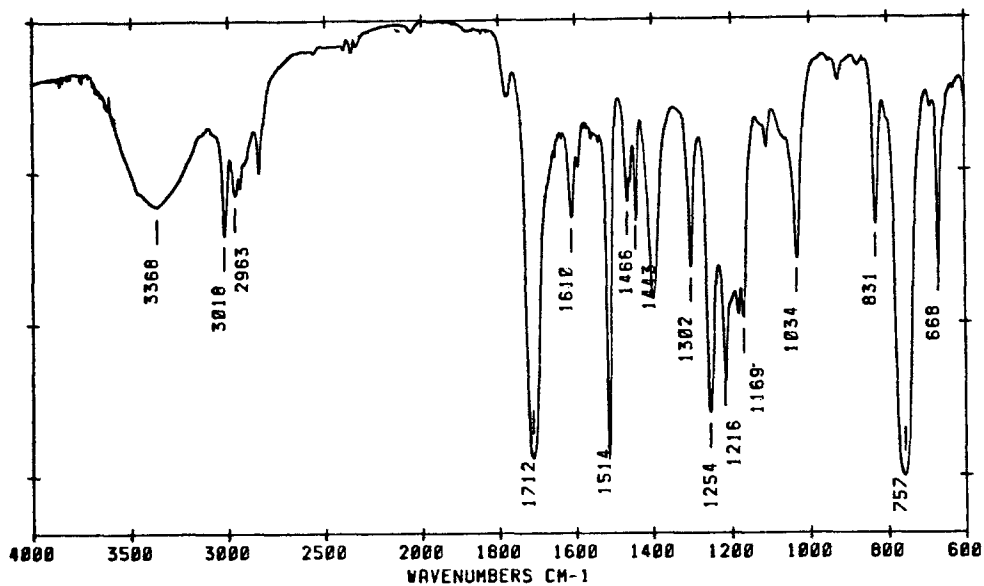


Figure 1. FT-IR spectrum of a p-MeOPhMI/HEA copolymer, (sample 1).

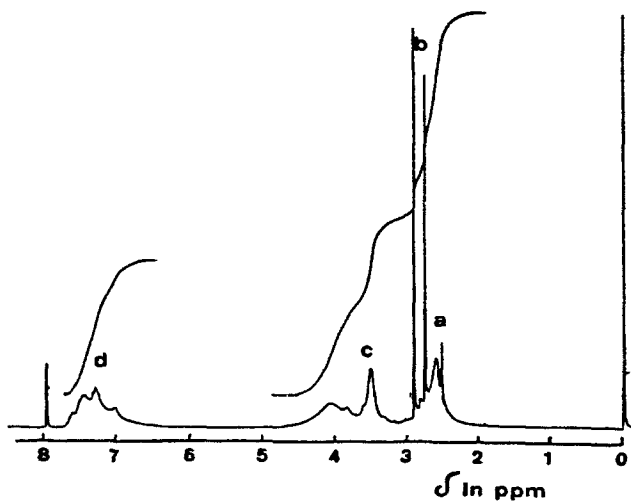


Figure 2. ^1H NMR spectrum of a N-PhMI/HEA copolymer, (sample 1, 250 MHz, room temperature, DMSO-d_6 , TMS).

The p-MeOPhMI/HEA copolymers show the following signals: **a** at $\delta=2.61$ - 3.09 assigned to $-\text{CH}_2\text{-N-CH}_2-$ and >CH-CH< ; **b** at $\delta=3.78$ corresponding to $-\text{CH}_2\text{-O-}$; and **c** at $\delta=6.83$ - 7.26 ppm attributed to aromatic protons. (see Fig. 3).

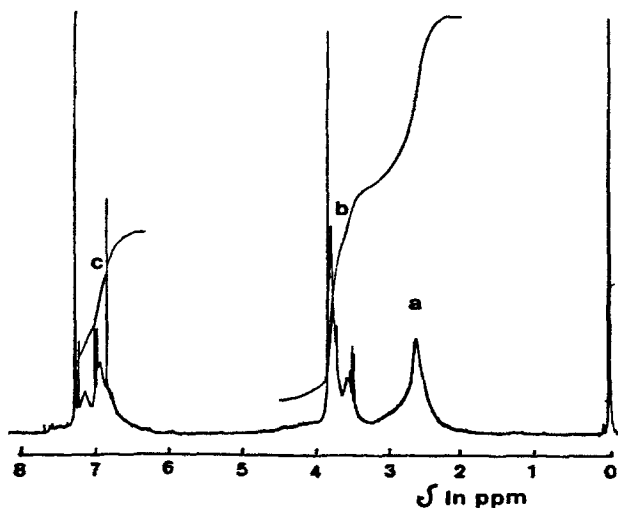


Figure 3. ^1H NMR spectrum of a p-MeOPhMI/HEA copolymer, (sample 1, 250 MHz, room temperature, DMSO- d_6 , TMS).

For N-PhMI/HEA and p-MeOPhMI/HEA copolymers, the copolymer composition was calculated by comparing the equivalent area of aromatic protons and methylene protons. Copolymer compositions were also determined from the N/C ratio which is unaffected by the occluded water in the copolymer. The values were in agreement. The copolymers are statistical products. The structure of the p-MeOPhMI/HEA copolymer is strongly affected by the initial composition of the comonomer structure. The 1.0:1.0 monomer ratio in the feed yields a statistical copolymer rich in HEA, due to the higher reactivity of the heterocyclic ring. By increasing the temperature at constant copolymerization time, the copolymer composition becomes alternating.

Alternating copolymers are produced if the copolymerization occurs only by "polyaddition" and for "polycondensation". But the present copolymers are somewhat different; they are statistical copolymers due to dipole-ion side reactions.

Due to the greater reactivity of p-MeOPhMI, copolymers were statistically richer in p-MeOPhMI/HEA.

The N-PhMI/HEA copolymers are richer in HEA, because of the nucleophilic attack of the nitrogen electron-pair on the aziridinium ion in $^+\text{MNME}^-$ which opens and produces a homodiad MNMN . In contrast, in the p-MeOPhMI/HEA system, statistical copolymers rich in ME were obtained. A homodiad of MEME is produced by the addition to the ME double bond.

The temperature affects only slightly copolymer composition.

ACKNOWLEDGEMENTS

The authors thank Dirección de Investigación, Universidad de Concepción (Grant N° 20.13.49).

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Accepted September 23, 1991 K