Polymer Bulletin 42, 281–286 (1999)

Polymer Bulletin
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Novel non-alternating copolymers synthesized by spontaneous copolymerization of *p*-chlorophenylmaleimide with 2-methyl-2-oxazoline

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Received: 27 September 1998/Revised version: 27 January 1999/Accepted: 28 January 1999

Summary

The copolymerization of p-chlorophenylmaleimide (**1**) as electrophilic monomer with 2-methyl-2-oxazoline (**2**) as nucleophilic monomer without initiator in solution under different experimental conditions was investigated. Copolymers were characterized by FT-IR and ^{1}H-NMR spectroscopy. The copolymer composition was determined from ^{1}H-NMR spectra. Molecular weights ranged between 1700 and 5400 g/mol by vapor pressure osmometry.

Keywords: Nucleophilic and electrophilic monomers; spontaneous copolymerization; non-alternating copolymers.

Introduction

Most of' the polymerization reactions require an initiator, catalyst or high energy radiation. However, the zwitterion polymerization describes the copolymerization in which two kinds of monomers interact with other to produce zwitterion intermediates leading to the production of statistical or alternating copolymers (1-15). As zwitterions are responsible for both initiation and propagation of these systems it is not necessary to employ an added initiator or catalyst to start the copolymerization.

An electrophilic monomer (M_E) and a nucleophilic one (M_N) are employed in this copolymerization. Spontaneous copolymerizations have been reported for nucleophilic monomers such as cyclic iminoethers with electrophilic monomers such as α,ß-unsaturated acids, lactones, maleimide derivatives, cyclic anhydrides.

The interaction between these two kinds of' monomers produce a "genetic zwitterion" 'M_NM_E which is responsible for both initiation and propagation.

$$M_N + M_E \longrightarrow {}^{+}M_NM_E^{-} \longrightarrow {}^{+}M_N(M_EM_N)_nM_E^{-}$$

An alternating copolymer is obtained if the propagation reaction involves only "polyaddition" and "polycondensation" reactions. It is possible that a lateral reaction may occur by interaction of the zwitterionic species with monomer, M_N or M_E leading to production of non-alternating copolymers.

The aim of this paper is to report the obtention of copolymer structures which cannot be synthesized by usual copolymerization reactions like radical or ionic polymerization,

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Experimental Part

Materials

4-Chlorophenylmaleimide **1** was synthesized by a published method (16). 2-methyl-2-oxazoline **2** (Aldrich Chem. Co.) was purified by destillation under N_2. Solvents were purified by usual methods (17).

Copolymerization

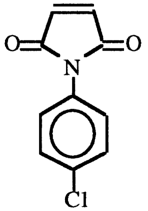
A set of 15 copolymerizations was performed keeping constant the total mole number of comonomers (**1** + **2** = 0.010 mole). In a polymerization glass tube, x **1** mole were dissolved in 10 mL of solvent just distilled and (0.01-x) **2** mole were added under N_2 using a syringe. The flask was introduced in a thermostated bath for the required time. The copolymer solution was added dropwise over 200 mL of diethyl ether and the precipitate was isolated by centrifugation, purified by reprecipitation and dried under vacuum at 30°C up to constant weight.

Measurements

The FT IR and ^1H NMR spectra were recorded with a Magna Nicolet 550 and a Bruker 250P Spectrometer respectively. The molecular weights were determined by a Knauer osmometer in acetone at 30°C.

Results and Discussion

According to spontaneous copolymerization concept, the copolymerization reaction of p-chlorophenylmaleimide (**1**) with 2-methyl-2-oxazoline (**2**) without initiator were carried out varying the initial composition between both monomers and keeping constant the total amount of substance (0.01 mole) (see Table 1).



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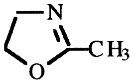

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Table 1. Conditions and results of **1** with **2** at 70°C in CH_3CN during 24 h.

Copolymer N°	Initial mole[a] ratio **1/2**	Mole ratio[b] $\frac{\text{m.u. of } \mathbf{1}}{\text{m.u. of } \mathbf{2}}$ in the copolymer	M_n[c] (g/mol)	Yield (%)
1	1 : 3	1.3 : 1.0	4.300	16
2	1 : 2	1.4 : 1.0	4.100	36
3	1 : 1	1.1 : 1.0	3.200	66
4	2 : 1	1.5 : 1.0	3.300	72
5	3 : 1	2.1 : 1.0	3.100	75

a) Total mol number of comonomers: 0.01.
b) Obtained from ^1H-NMR spectra
c) Determined by vapor pressure osmometry in acetone at 30°C.

All the copolymers were soluble in organic solvents as acetone, DMSO, DMF.

The conversion varied between 16 and 75% depending on the comonomer ratio in the feed. The conversin determined from the fractino insoluble in diethyl ether, increased on raising the amount of electrophilic monomer in the feed. The highest conversion was obtained for a 3:1 ratio of monomers **1:2** (75%). Table 2 shows the influence of the copolymerization time, temperature, and solvent on the copolymer composition, molecular weight, and yield. It can be concluded that there is a preferential increase of m.u. of **1** in the copolymer at the first period (72 h) of copolymerization. Between 96 and 120 h of copolymerization, the copolymer composition remains approximately constant (near to 1:1). The increase of the molecular weight by time was as expected. Table 2 (copolymers **9** and **12**) also shows that the solvent polarity has a significant influence on the yield or on the copolymer composition but does not have a significant effect on the molecular weight. An increase of the temperature (see Table 2, copolymers **9**, **13**, and **14**) increased significantly the yield (40, 50, and 80% respectively) but not the molecular weight. This increase produces also an important effect on the incorporation of the monomer units favoring the incorporation of m.u. **2**.

The FT-IR of the copolymers show, among other signals absorption, bands at 1721 and 1643 cm^{-1} corresponding to νC=O imide from **1** and νC=O amide group from **2** which confirm the opening of oxazoline ring. The FT-IR spectra of the copolymers rich in m.u. of **1** (e.g. copolymer **5**) show intensive bands of –CO-N-CO- of 1721 cm^{-1} but in copolymers rich in m.u. of **2** or near to 1:1 (e.g. copolymer **3**) there is an important increase in the intensity of the –CO-N<band at 1644 cm^{-1}. (see Figure 1)

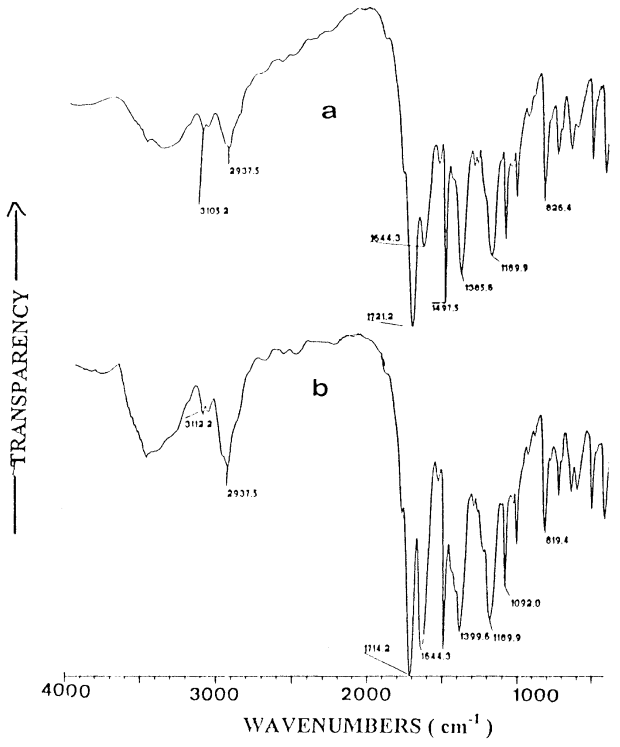


Figure 1. FT IR spectra of the copolymers from **1** and **2**, (a) sample N°3 and (b) sample N°5.

Table 2. Influence of the copolymerization time, temperature, and solvent on yield, molecular weight and composition of the copolymer for the copolymerization of **1** with **2** (ratio in the feed 1:1).

Copolymer N°	Copolymerization time (h)	Copolymerization temperature (°C)	Solvent (5 ml)	M_n a) (g/mol)	Mol ratio b) m.u. of **1** / m.u. of **2** in the copolymer	Yield (%)
6	6	70	CH3CN	1.700	2.2 : 1.0	12
7	12	70	CH_3CN	3.180	1.9 : 1.0	36
8	24	70	CH_3CN	3.200	1.6 : 1.0	66
9	72	70	CH_3CN	3.600	1.5 : 1.0	80
10	96	70	CH_3CN	4.600	1.0 : 1.03	87
11	120	70	CH_3CN	4.700	1.0 : 1.08	89
12	72	70	Benzene	3.800	1.0 : 1.2	11
13	72	60	CH3CN	3.700	1.6 : 1.0	50
14	72	50	CH3CN	3.650	2.1 : 1.0	40
15	120	50	CH3CN	5.400	2.1 : 1.0	51

a) Determined by vapor pressure osmometry in acetone at 30°C

b) From ^{1}H-NMR spectra.

On the other hand, the ^{1}H-NMR spectra of the copolymers show remarkable dependence of their composition on the initial comonomer composition. For example, the signal intensity at δ = 2.1 ppm corresponding to methyl protons of m.u. of **2**, decreases with increasing content of m.u. of **1**. As an example, the figure 2 shows the ^{1}H NMR spectrum of sample 3.

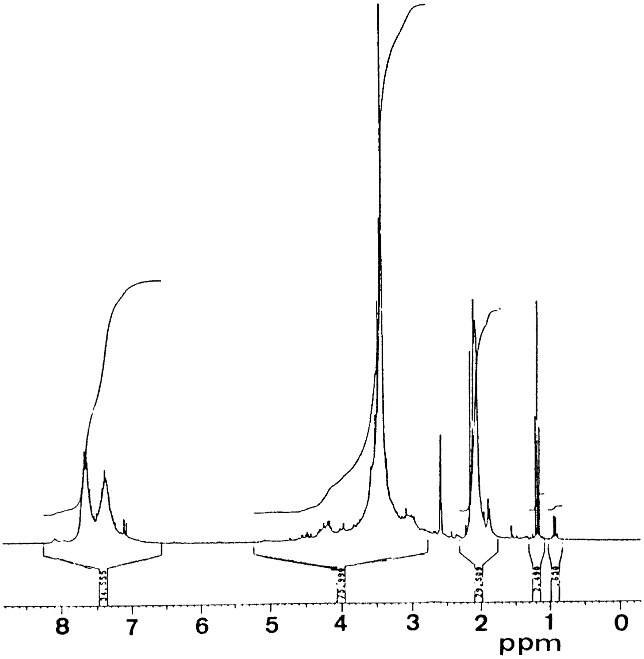
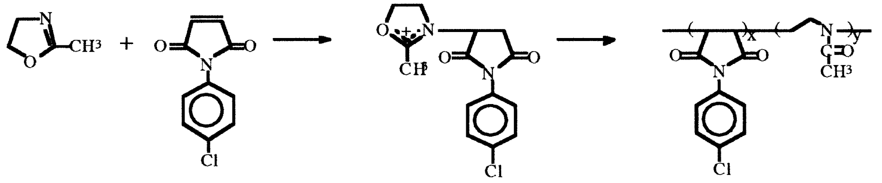


Figure 2. ^{1}H NMR spectrum (250 MHz, room temperature, TMS, $CDCl_3$ of the copolymer from **1** and **2**, sample 3, obtained at 70°C in CH_3CN by 24h).

The copolymer composition was determined by comparison of the aromatic protons area between 7.2 and 7.9 ppm which corresponds to the m.u. of **1** and the methyl protons area centered at $\delta = 2.1$ ppm from the m.u. of **2**. The signal at 3.5 ppm is attributed to $-CH_2N$. There is not a signal between 5.0 and 7.0 corresponding to CH=CH protons, indicating that the copolymerization occurred involving the double bond of maleimide moiety but not with opening ring through imide bonds.

For the copolymerization mechanism, according to these results it is possible to suggest the involvement of the "genetic zwitterion".



2 **1** $^+M_NM_E^-$ non-alternating copolymer,

x ≠ y

Thus, the interaction between **1** and **2**, produces a "genetic zwitterion" $^+M_NM_E^-$, which is the specie responsible for the growth reaction.

The present copolymers are non-alternating because there are side reactions of dipole-ion. For **1/2** system rich in M_N there is a nucleophilic attack of electron-pair of the nitrogen atom of **2** on $^+M_N(M_EM_N)_nM_E^-$ opening the ring and producing a homodiad $^+M_NM_N\sim$. On the other hand, for those copolymers **1/2** rich in M_E non-alternating copolymers are also produced by addition of $^+M_N(M_EM_N)_nM_E^-$ to the double bond of M_E yielding a homodiad $\sim M_EM_E^-$. It is not possible to discard completely other copolymer unit-structures, but no evidence was observed by the analysis of FT-IR and ^{1}H-NMR spectra.

In conclusion, non-alternating copolymers were synthesized by spontaneous copolymerization of p-chlorophenylmaleimide with 2-methyl-2-oxazoline. The yield of the solution copolymerization depended on the feed monomer ratio, temperature, and time of copolymerization as well as of the solvent polarity. In benzene the lowest copolymerization yield (11%) and the highest in CH_3CN at 70°C, were obtained. By increasing the copolymerization time from 6 to 120 h, the yield increased from 12% to 89%. The molecular weight varied from 1.700 to 5.400 being the lowest values but it is a characteristic of the spontaneous copolymerization. Almost all the copolymers were richest in p-chlorophenylmaleimide monomer units, indicating the presence of the dipole-ion reaction, between the zwitterion species and monomer **1**. Only for equimolar feed monomer ratios in CH_3CN, 70°C, 96 h and 120 h, were obtained copolymers with a copolymer composition close to 1:1.

Acknowledgements

The authors thank to Dirección de Investigación, Universidad de Concepción for financial support.

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