"Spontaneous Copolymerization of *p*-Chlorophenylmaleimide with 2-Methylaziridine"

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p-Chlorophenylmaleimide as an electrophilic monomer was copolymerized in the absence of initiator with 2-methylaziridine as nuclephilic monomer. The copolymers were characterized by elemental analysis, FT-IR, and ^{1}H-NMR spectroscopy. The copolymer compositions were determined by chloro elemental analysis and ^{1}H-NMR spectroscopy. 2-Methylaziridine is more reactive than p-chlorophenylmaleimide yielding statistical copolymers. Mn, determined by vapor pressure osmometry, varied between 3.000 and 6.700 g/mol.

INTRODUCTION

The zwitterion polymerization describes the copolymerization in which two kinds of monomers interact with other to produce zwitterion intermediates leading to the production of statisticals or alternating copolymers (1–20). As zwitterions are responsible for both initiation and propagation of these systems, it is not necessary to employ an initiator or high-energy radiation to start the copolymerization.

Two kinds of monomers, an electrophilic monomer (M_E) and an electrophilic one (M_N), are employed in this copolymerization. The general scheme is given as follows:

$$M_E + M_N \rightarrow {}^-M_E - M_N^+$$

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$$1 + 1 \rightarrow {}^-M_E - M_N M_E - M_N^+$$

$$2 + n1 \rightarrow {}^-M_E - (M_N M_E)_{n+1} - M_N^+$$
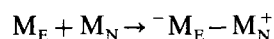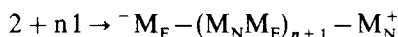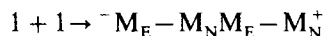
The zwitterion intermediate 1 which is the so-called genetic zwitterion and responsible for both initiation and propagation.

In the later stages of copolymerization, when the concentration of macro-zwitterion is higher, the reaction between two macrozwitterions is favored:

$${}^-M_E(\sim)_n M_N^+ + {}^-M_E \sim (\sim)_m M_N^+ \rightarrow {}^-M_E(\sim)_n M_N M_E(\sim)_m M_N^+$$

which yield a sharp increase of the molecular weight. If the growth reaction involves only "polyaddition" and "polycondensation" reactions, an alternating copolymer is obtained. It is also possible that lateral reactions may occur by interaction of the zwitterionic species with monomer, M_N or M_E, leading to production of statistical copolymers.

It is well known the very good properties of N-phenylmaleimide and derivatives as electrophilic monomer as well as their thermal properties (16–20). Due to that we report now the synthesis without initiator of copolymers employing p-chlorophenlymaleimide as M_E monomer and 2-methylaziridine as M_N monomer.

EXPERIMENTAL

Monomers

2-Methylaziridine, MAz (from Aldrich) was purified by distillation under nitrogen. p-Chlorophenylmaleimide p-ClPhMI, was synthesized and purified by a published method (16). Solvents were purified by the usual methods (17).

Copolymerization

In a glass tube, a mixture of MAz with p-ClPhMI was dissolved in CH_3CN (5 ml) under N_2. The tube was kept at the reaction temperature for the required time. The copolymer was precipitated in diethyl ether, separated by centrifugation, purified by reprecipitation and dried under vacuum. The yield of copolymers was determined gravimetrically. The composition of the copolymers was determined by measuring the intensity of the specific reso-

nances for the respective monomer units in the ^{1}H-NMR spectra as well as by elemental analysis.

Measurements

^{1}H-NMR spectra were taken on a Bruker AC-250 spectrometer in CDCl$_3$ at room temperature, c.a. 27°C, FT-IR spectra were recorded on a Nicolet Magna 550 spectrophotometer. Number-average molecular weights (M̄n) were determined by Knauer vapor pressure osmometer calibrated with benzil, at 30°C using CHCl$_3$ as solvent. Thermogravimetric analysis (TGA) was carried out in a nitrogen stream with a heating rate of 10°C/min by using a DSC/TGA-STA 625 Polymer Laboratories. Samples (1–4 mg) were heated in a platinum sample holder between 20°C and 550°C.

RESULTS AND DISCUSSION

Copolymerizations of MAz and p-ClPhMI were carried out at various feed mol ratios and time of copolymerizations, for mixed total amount of comonomers (see Table I).
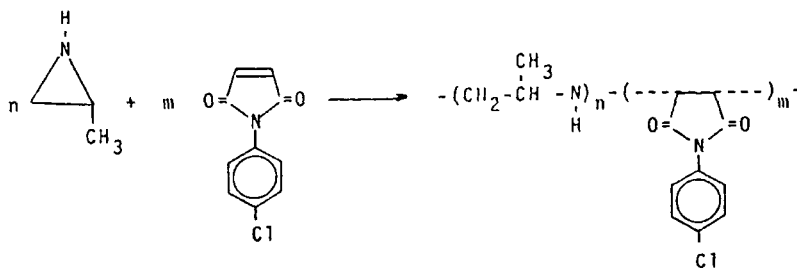
All the copolymers, MAz/p-ClPhMI were soluble in organic solvents as CHCl$_3$, DMSO, DMF.

The conversion varied between 21 and 61% depending on the comonomer ratio in the feed and the copolymerization time (see Fig. 1). The conversion, determined from the fraction insoluble in diethyl ether, increased on raising the amount of nucleophilic monomer in the feed. The highest conversion was obtained for a 3:1 ratio of comonomers MAz/p-ClPhMI (31%) (see Table I). There is a dependence of comonomer ratio in the feed and the copolymer composition (see Fig. 2). The curve indicates that the copolymerization is near to be statistical and it has an azeotropic
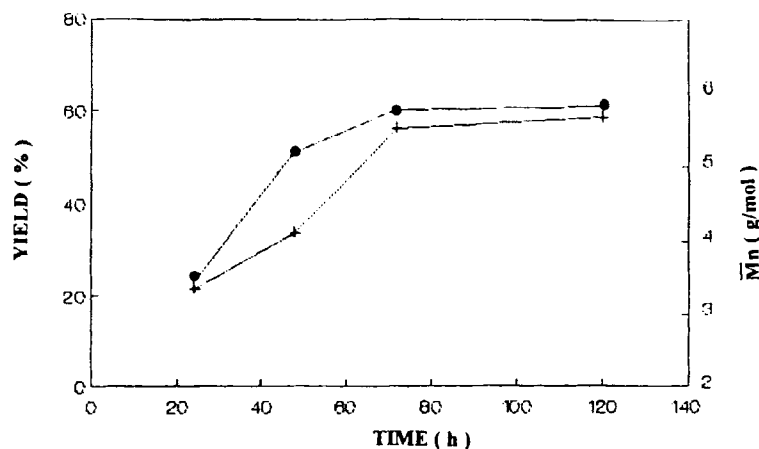
FIGURE 1   Relationship between the copolymerization time with the yield and molecular weight.

TABLE I   Conditions and results of solution copolymerization (in CH_3CN), of MAz with *p*-ClPhMI at 70 C

Copolymer Sample	MAz (mmol)	p-ClPhMI (mmol)	Time (h)	Yield (%)	$\bar{M}n \cdot 10^{-3}$ (g/mol)	Copolymer Composition MN/ME from:	
						Elemental analysis	^1H-NMR
1	7.5	2.5	24	14	3.07	3.30 : 1.00	3.34 : 1.00
2	6.6	3.4	24	18	3.20	2.32 : 1.00	2.27 : 1.00
3	5.0	5.0	24	23	3.35	1.70 : 1.00	1.61 : 1.00
4	3.4	6.6	24	25	3.60	1.00 : 1.60	1.00 : 1.55
5	2.5	7.5	24	31	3.80	1.80 : 1.82	1.00 : 1.85
6	5.0	5.0	48	51	4.10	1.73 : 1.00	1.00 : 1.68
7	5.0	5.0	72	60	5.50	1.81 : 1.00	1.00 : 1.73
8	5.0	5.0	120	61	5.65	1.85 : 1.00	1.00 : 1.77

point, so in principle both copolymerization parameters are less than unity. It shows a point where the copolymer and feed compositions are the same and the copolymerization proceeds without change in the feed composition. For this copolymerization, it occurs at MAz/*p*-ClPhMI ratio of 0.6.

The molecular weight, $\bar{M}n$ decreases as the MAz units increase in the copolymer, due to their lowest molecular weight and it increases by increasing the copolymerization time up to a near constant value of $5.50-5.65 \cdot 10^{-3}$ g/mol for copolymer composition 1.81:1.0 and 1.85:1.00 respectively (see Fig. 1).

The monomer reactivity ratios were determined by the least-squares method according to Fineman-Ross (F-R) (23) and by the Kelen-Tüdos
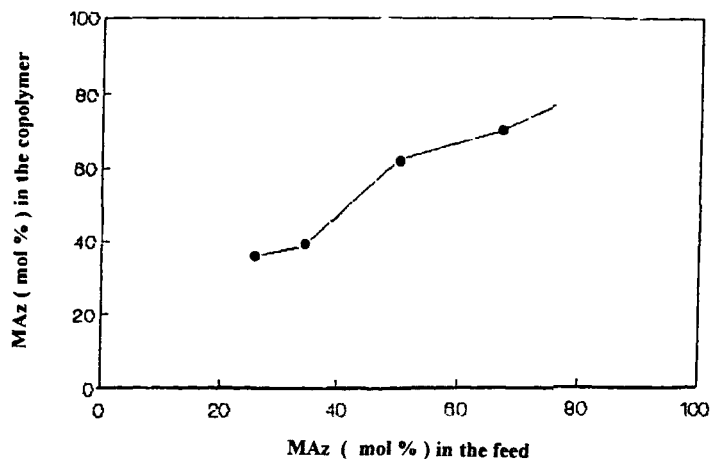
FIGURE 2 Dependence of the copolymer composition on the relative amount of MAz in the initial mixture for the copolymerization of MAz with p-ClPhMI at 70°C in CH₃CN.

(K-T) method (24) (see Table II). MAz and p-ClPhMI correspond to monomer 1 and 2 respectively (see Table II). It shows the greater tendency of MAz monomer to produce a homodiade than that p-ClPhMI. Both methods present a discrepancy, particularly for r_2, but the copolymer can be considered as random copolymer.

The FT-IR spectra of the copolymers show among others, absorption bands at 2972.4 cm⁻¹ corresponding to the v_{C-H} of the MAz, at 1721.2 cm⁻¹ corresponding to $v_{C=O}$ imide group from p-ClPhMI which confirms the opening of aziridine ring (see Fig. 3).

Figure 4 shows the 250 MH$_z$ ¹H-NMR spectra of the copolymer 3. At up-field, 1.18 ppm, the methyl proton signal of MAz units appears.

The signal about 5 and 5.5 ppm which allows the assumption that the methylaziridinic ring of the zwitterion is opened by only one way when it is

TABLE II Monomer reactivity ratio r_1 and r_2 by the Fineman-Ross (F-R) and Kelen-Tüdos $(k - T)$ methods for MAz/p-ClPhMI copolymer

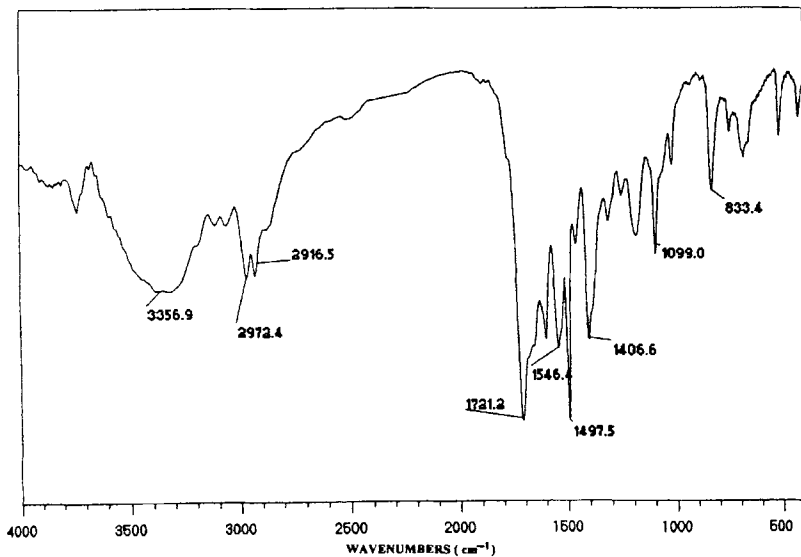| Method	r_1	r_2	$r_1 - r_2$
F-R	0.98	0.56	0.55
K-T	0.95	0.46	0.44

FIGURE 3   FT-IR spectrum of the poly(2-methyl aziridine-*co*-*p*-chlorophenyl-maleimide) sample 3.
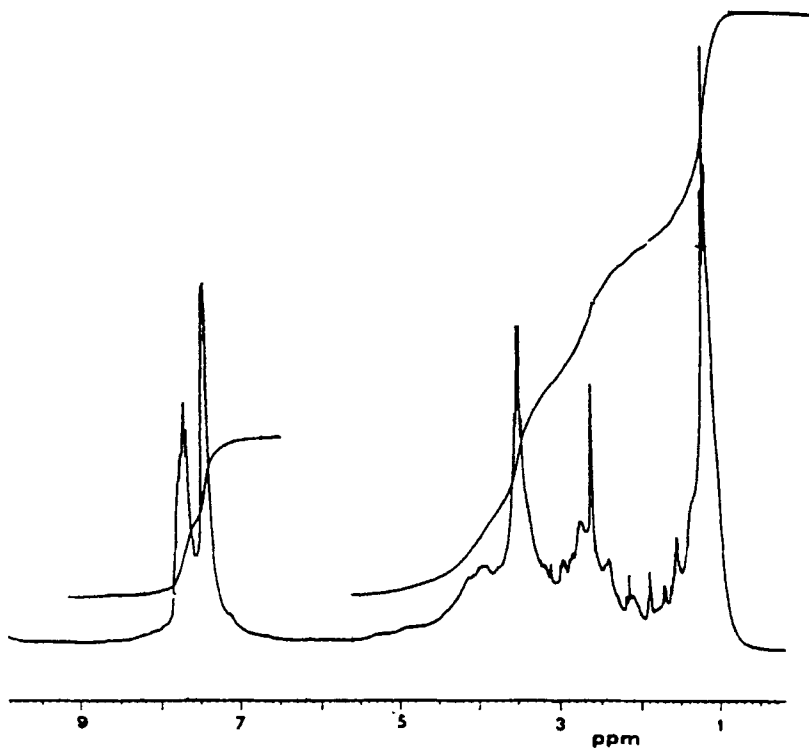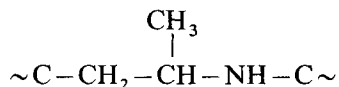

FIGURE 4 ^{1}H-NMR spectrum (250 MHz, CDCl$_3$, TMS, room temperature) of poly(2-methylaziridine-*co*-*p*-chlorophenylmaleimide), sample 3.

attacked by the carbanion of a second zwitterion yielding the following partial structure is not present.

$$\sim C - CH_2 - \overset{\overset{\displaystyle CH_3}{\displaystyle |}}{CH} - NH - C \sim$$

The copolymer composition was determined by comparison of the aromatic protons area between 7.2 and 7.9 ppm which corresponds to the units of p-ClPhMI and the methyl protons area centered at $\delta = 1.18$ ppm.

Copolymerization Mechanism

The interaction between M_N (MAz) (p-ClPhMl), produces a "genetic zwitterion" ($^-M_E M_N^+$) which is the specie responsible for the growth reaction:
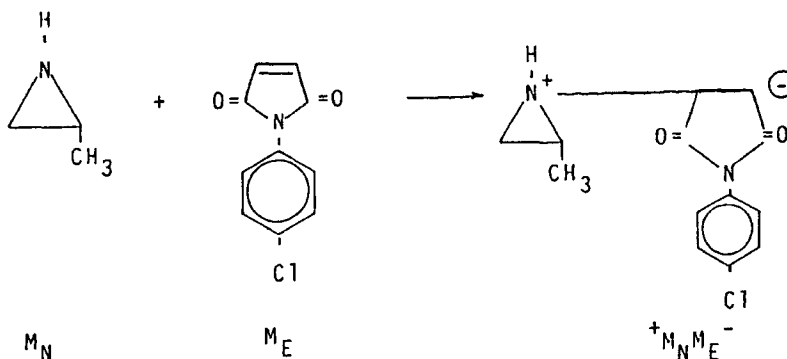
The present copolymers are statistical because there are side reactions of dipole-ion.

For MAz/p-ClPhMl system rich in M_N, there is a nucleophilic attack of the electron-pair of the nitrogen atom of the MAz on $^+M_N M_E^-$ opening the ring and producing a homodiade $^+M_N M_N^+$:
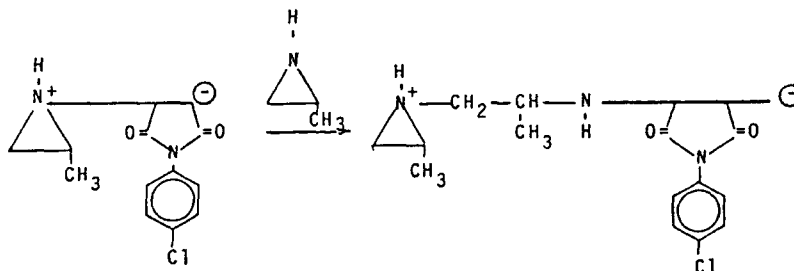
On the other hand, for those copolymers MAz/p-ClPhMI rich in M_E, statistical copolymers are also produced by addition to the double bond of M_E yielding a homodiade $^-M_EM_E^-$:

Thermal Behavior

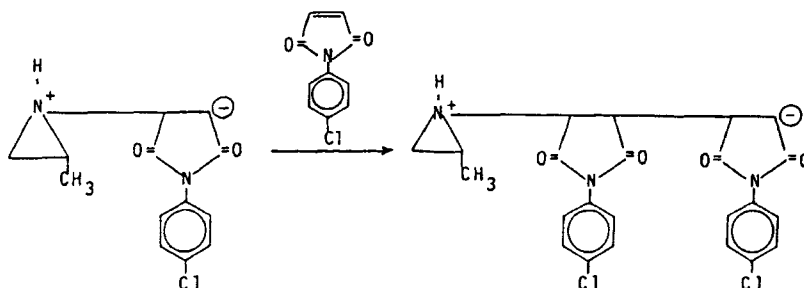The thermal behavior of MAz/p-ClPhMI copolymer was examined by thermogravimetric analyses (TGA) in nitrogen at a heating rate of 10°C/min. Table III shows the weight-loss at different temperatures. All the copolymers are stable up to 200°C and the thermal stability increases with increasing content of the p-ClPhMI unit in the copolymer (see Table III).

Determination of the Kinetic Parameters

The thermal decomposition kinetics of the thermogravimetric weight loss was determined using (25):

$$- d\alpha/dt = K_n(1-\alpha)^n$$

TABLE III   Weight-loss at different temperatures and kinetic parameters for the degradation of MAz/p-ClPhMI copolymers

Copolymer	Copolymer Composition[a] MAz/p-ClPhMI	Weight-loss at different temp.(°C)					Ea (kJ·mol^{-1})	A (s^{-1})
		100	200	300	400	500		
1	3.34 : 1.00	0.0	8.9	44.2	76.7	88.4	25.12	0.0642
2	2.27 : 1.00	0.0	4.3	33.3	63.2	76.8	30.54	0.1639
3	1.61 : 1.00	0.0	1.2	19.5	64.5	80.2	35.66	0.5720
4	1.00 : 1.55	0.0	1.0	12.5	48.7	65.9	40.79	0.6743
5	1.00 : 1.85	0.0	1.0	13.9	50.1	64.8	46.68	2.8352

[a] Calculated from ^{1}H-NMR spectra. See Table I.

K_n is the specific rate and was obtained using the Arrhenius relation

$$K_n = A_{exp}(-E/RT)$$

A is the pre-exponential coefficient. Combining both equations and adopting the logarithmic form the following is obtained:

$$\beta = \ln[-d\alpha/dT/[v(1-\alpha)^n]] = \ln A - (E/RT)$$

A linear multiple regression program was used to calculate the kinetic parameters E and A. Plotting β vs $1/T$ should give a straight line, and E and A are determined from the slope and intercept (see Fig. 5). For all the copolymers, the program was run for $n=0$ and $n=1$. The linear relationships obtained indicated that the reaction is of order 0. The coefficients of linear correlation varied from 0.992 to 0.999. The kinetic parameters E and
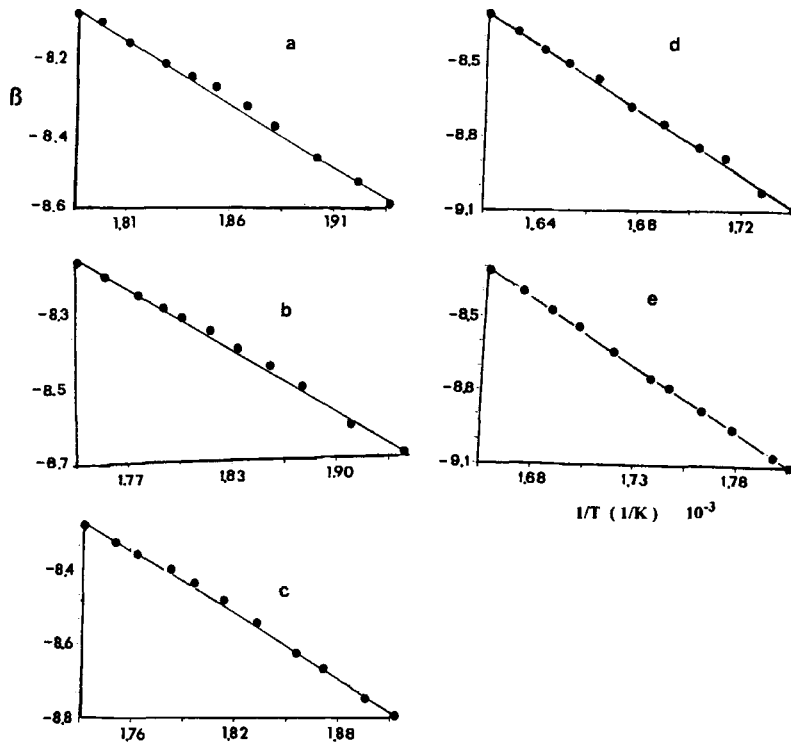

FIGURE 5   Arrhenius plot for the degradation of poly(2-methylaziridine-co-p-chlorophenyl-maleimide), copolymers 1 (a); 2 (b); 3 (c); 4 (d); and 5 (e).

A calculated from these plots are collected in Table III for comparative purposes.

CONCLUSIONS

Statistical copolymers were synthesized by spontaneous copolymerization of 2-methylaziridine as nucleophilic monomer and *p*-chlorophenylmaleimide as electrophilic monomer. The yield of solution copolymerization was low due to a poor interaction between both monomers to produce a "genetic zwitterion". It was lower than those obtained previously with acrylic and methacrylic acid, which showed a highest electrophilic reactivity (15).

All the copolymers are thermally stable up to about 200°C and the thermal stability increases by increasing the *p*-ClPhMI content. For all the copolymers considered, the decomposition reaction was found to be zero order, implying that, if the sample mass is increased, the rate of decrease in mass remains unchanged at a specified temperature.

Acknowledgements

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