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Copolymerization via zwitterion

18. N-Phenylmaleimide with ethyleneimine

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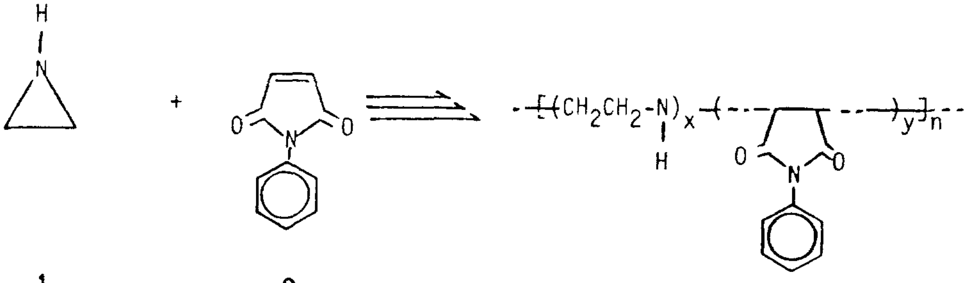
SUMMARY

Copolymers of N-phenylmaleimide and ethyleneimine were synthesized in acetonitrile in the absence of initiator. The copolymers are insoluble in solvents such as DMF, $CHCl_3$, DMSO, CH_3OH, H_2O. The copolymer composition as determined by elemental analyses depends on the initial monomer ratio. The thermal stability of copolymers was studied.

INTRODUCTION

In the course of studies on the spontaneous copolymerization of cyclic iminoethers and ethyleneimine, nucleophilic monomers (MN) toward electrophilic-ones (ME) such as β-propiolactone (1), β-butyrolactone (2), methacrylic acid (3), acrylic acid (4-5), N-phenylmaleimide and their derivatives (6-9)have been used. The interaction between MN and ME induced the "spontaneous copolymerization" to give alternating or statistical copolymer's via zwitterion intermediates $^+$MNME$^-$. Usually this "genetic zwitterion" is responsible not only for initiation but also for the propagation reaction.

The present paper reports the copolymerization of N-phenylmaleimide (PhMI) **2** as electrophilic monomer and ethyleneimine (EI) **1** as nucleophilic monomer to statistical copolymers



1 **2** **3**

EXPERIMENTAL

Materials: N-phenylmaleimide was synthesized according to the literature (10). Ethyleneimine (Fluka) was purified by distillation from KOH. The solvents were purified according to usual methods (11).

Copolymerization: In a glass tube, a mixture of PhMI and EI (0.04 mol) was dissolved in 10 ml solvent under $N_2(g)$. Then the flask was kept at 60°C for 24 h. The copolymerization mixture was homogeneous during the reaction. It was poured in diethylether to precipitate a polymeric material which was purified by repeated reprecipitation and then dried in vacuo. In a similar way the copolymerizations at different time and copolymerization solvents were carried out.

Measurements: The IR spectra (KBr) were recorded on a Perkin Elmer 577 Spectrophotometer. The thermal stability was examined by a Thermobalance Perkin Elmer TGS-1.

RESULTS AND DISCUSSION

It is well known that ethyleneimine **1** polymerized to poly(iminoethylene) with various cationic catalyst (12) and N-phenylmaleimide **2** and derivatives polymerize with anionic initiator (13). On the other hand, both monomers have been copolymerized with different comonomers throught copolymerization via zwitterion (6-9, 14-15).

Now, copolymerizations were carried out at different mole ratios but keeping the total amount of comonomers constant (0.040 mol). The copolymers are insoluble in solvents as DMF, DMSO, $CHCl_3$, ethanol, H_2O. The copolymerization conditions are summarized in Table 1.

Table 1. N-phenylmaleimide (PhMI) with ethyleneimine (EI) at 60°C by 24 h.

Copolymer	Feed mole ratio[a)] **1** : **2**	Yield (%)	N/C[b)] ratio	Copolymer Composition[b)] **1** : **2**
1	0.33:1.00	22	0.1492	0.38:1.00
2	0.48:1.00	30	0.1514	0.40:1.00
3	1.00:1.00	36	0.2085	1.22:1.00
4	2.00:1.00	51	0.2633	2.29:1.00
5	3.00:1.00	58	0.3512	5.07:1.00

[a)] Total amount: 0.04 mol
[b)] From elemental analyses

The copolymer composition show a strong dependence of the feed mole ratio. This behaviour also can be observed in Fig.1. The EI incorporated in the copolymer is proportional to the EI mole in the feed.

This copolymer system represents a nearly ideal statistical copolymerization.

The copolymerization yield increases as the EI incorporation in the copolymer increases. The highest yield is obtained for the copolymer richest in EI (copolymer 5).

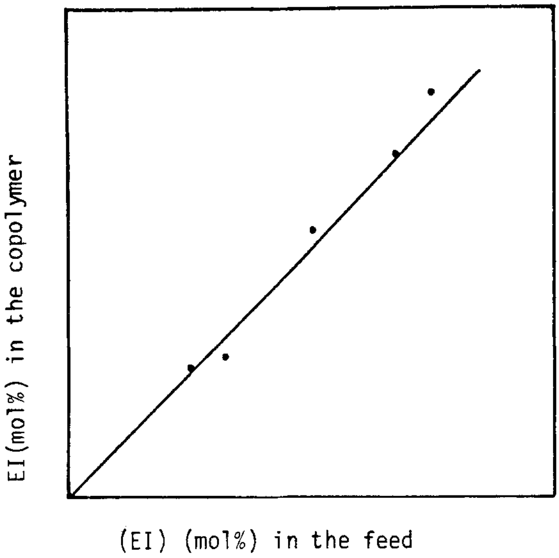


Figure 1. Copolymer composition curve of the N-phenylmaleimide-ethyleneimine copolymerization (slope: 1.145; σ^2=0.9915; intercept: 4.4936)

Also, reactions with different solvents and times of copolymerization were carried out. (See Table 2 and 3).

Table 2. Effect of the dielectric constant (ε) on the yield and copolymer composition. Copolymerizations were performed with a 3.00:1.00 monomer mol ratio in the feed at 50°C for 24 h.

Copolymer	Solvent (5ml)	ε	Yield (%)	N/C[a] ratio	Copol.Composition[a] **1** : **2**
6	CH_3CN	37.5	48	0.3325	4.30 : 1.00
7	CH_3COCH_3	20.7	30	0.2734	2.50 : 1.00
8	C_6H_6	2.3	25	0.2180	1.30 : 1.00

a) From elemental analyses

The more polar solvent CH_3CN gave the highest yield and it favors the incorporation of the more polar monomer **1** producing a statistical copolymer rich in **1** (See Table 2, copolymers 6).

Extending the time of copolymerization increases the yield and the **1** incorporated to the copolymer (See table 3, copolymer 12).

Table 3. Effect of the copolymerization time on the yield and copolymerization composition. Copolymerizations were carried out in CH_3CN with a 1.00:1.00 monomer mol ratio in the feed at 35°C.

Copolymer	Copol.Time (h)	Yield (%)	N/C ratio[a)]	Copol.Compos.[a)] **1** : **2**
9	6	11	0.1806	0.79 : 1.00
10	12	14	0.1839	0.84 : 1.00
11	24	18	0.2035	1.14 : 1.00
12	48	20	0.2042	1.16 : 1.00

[a)] From Elemental analyses

Since the copolymers are insoluble in common organic solvents they were characterized only by IR spectroscopy. The IR spectra of the copolymers show an absorption band at 1700cm^{-1} corresponding to νC=O (anhydride) but not the typical absorption band at 820cm^{-1} corresponding to conjugated double bond with the carbonyl group (See Fig. 2).

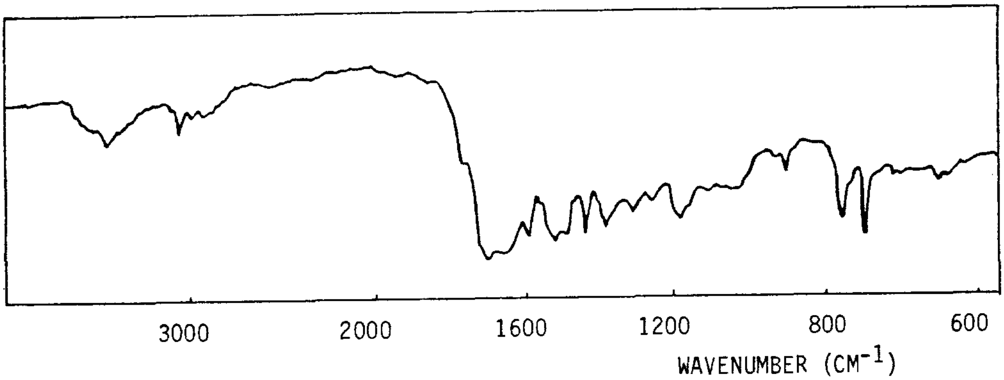


Figure 2. IR spectrum (KBr) of the copolymer sample 2.

In regard to the growth mechanism (since the copolymer composition is dependent of the feed monomer ratio) we suggest that the nucleophilic monomer **1** adds to the double bond of the **2** giving a zwitterion which growths to statistical copolymer by dipole-dipole and dipole-ion reaction.

Finally, the thermal stability for all copolymers was examined (See Table 4).

Table 4. Thermogravimetric analyses of the copolymers **1** : **2**

Copolymer	Copol.Comp.a)	weight loss at various temperatures (%)				
	1 : **2**	100°C	200°C	300°C	400°C	500°C
1	0.38:1.00	0	0.68	8.20	23.20	53.60
2	0.40:1.00	0	0.84	10.50	33.20	58.80
3	1.22:1.00	0	1.53	12.40	48.80	59.90
4	2.29:1.00	0	2.75	24.20	50.00	61.70
5	5.07:1.00	0	1.42	24.50	51.40	62.60
6	4.30:1.00	0	2.14	26.41	50.10	63.25
7	2.50:1.00	0	4.65	30.81	52.32	65.12
8	1.30:1.00	0	3.05	27.98	60.45	71.75
9	0.79:1.00	0	0.68	8.20	23.20	53.60
10	0.84:1.00	0	2.24	16.90	47.70	57.30
11	1.14:1.00	0	0.92	17.10	45.60	62.20
12	1.16:1.00	0	2.79	18.40	47.30	66.20

a)From elemental analyses.

All the copolymer are stable up to nearly 200°C. In general, the copolymer richer in EI show a less thermal stability.

ACKNOWLEDGMENTS

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