Polymer Bulletin 14, 79–83 (1985)

Polymer Bulletin

Spontaneous Copolymerization of 2-Methyl-2-Oxazoline and N-Phenyl Maleimide

Cristofor I. Simionescu, Mircea Grigoras, Elena Bîcu, and Geta Onofrei

"P. Poni" Institute of Macromolecular Chemistry, Alley Gr. Ghica Vodă no. 41A,
RO-6600-Jassy, Romania

SUMMARY

The copolymerizations of 2-methyl-2-oxazoline and N-phenyl maleimide in bulk or in solution,at 60°C or room temperature are reported. The initiation is spontaneous and is due to the formation of zwitterion by interaction of the two monomers. The copolymers are statistical,more rich in maleimide units and propagation reaction can take place both by anions and zwitterions.

INTRODUCTION

The spontaneous copolymerization of cyclic imino ethers as nucleophilic monomers with various electrophilic comonomers was studied for the first time by Saegusa and coworkers (1). As electrophilic monomers, β-propiolactone (2),methacrylic acid (3),acrylic acid (4),acrylamide (5) ethylensulfonamide (6),succinic anhydride (7) and phtalic anhydride (8) have been used. In all cases it has been assumed that the initiation takes place via zwitterion intermediate resulted from interaction of the two monomers leading to alternating or statistical copolymers.

The polymerization of maleimide and its derivatives in the presence of amines was reported too (9). In this case,the homopolymerization took place by anionic mechanism and was initiated by a zwitterion formed between maleimide and amine.

The present paper reports the copolymerization of N-phenyl maleimide as electrophilic monomer with 2-methyl-2-oxazoline as nucleophilic monomer. The copolymerization is spontaneous,takes place even at room temperature and leads to statistical copolymers richer in maleimide units.

EXPERIMENTAL

Materials: 2-Methyl-2-oxazoline (Oxz),commercial product,was purified by distillation under argon. N-phenyl maleimide (PhMI) was synthesized from maleic anhydride and aniline in a two stage reaction according to the original method developed by Searle (10). Acetonitrile was distilled over P_2O_5,under argon.

Copolymerization: The copolymerization reactions were carried out in sealed ampoules,in inert atmosphere,in solution or bulk. Few minutes after mixing of the two comonomers an intense red colour appears. The copolymerization system remains homogeneous durring the copolymerization, with exception of sample 3 (Table 1) which becomes solid. The copolymers were precipitated in diethyl ether,separated and dried.

Copolymer characterization: The IR (KBr pellets) and ^{1}H-NMR ($CDCl_3$) spectra were recorded on Perkin Elmer 577 and JEOL C60HL (60MHz) spectrophotometers, respectively. The molecular weights were determined by osmometry using a Knauer type vapour pressure osmometer (THF as solvent).

RESULTS AND DISCUSSION

The polymerization data of PhMI in the presence of Oxz are presented in Table 1.

Table 1: Copolymerization of 2-methyl-2-oxazoline (Oxz) with N-phenyl maleimide (PhMI)

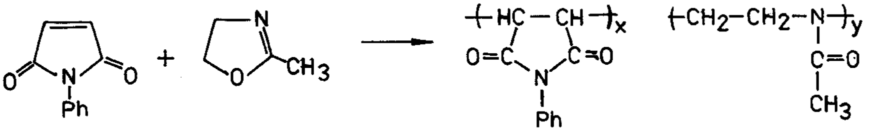
No	PhMI (g)	Oxz (g)	PhMI/Oxz (mol.ratio)	Solv.[a] (ml)	Temp. (°C)	Time (h)	Conv.[b] (%)	M_n	N (%)	Oxz[c] (mol%)
1.	1	2.5	1:5	(d)	20	75	3.2	-	10.2	26.5
2.	1	0.5	1:1	3	20	75	32.2	1019	8.8	11.0
3.	1	0.5	1:1	(d)	60	24	80.6	2416	11.6	42.0
4.	1	2.5	1:5	(d)	60	24	32.5	973	10.8	32.0
5.	1	0.5	1:1	3	60	24	70.3	894	10.5	28.5

a) The copolymerizations were carried out in solution (acetonitrile) or in bulk (d)

b) Conversion was determined for diethyl ether insoluble fraction

c) Copolymer composition was estimated by ^{1}H-NMR spectroscopy and elemental analysis.

The obtained products, according IR, ^{1}H-NMR spectra and elemental analysis data are copolymers with x > y.



(PhMI) (Oxy)

The copolymers are white-pink coloured, soluble in CH_3CN, $CHCl_3$, THF, 1.4-dioxane, DMSO, benzene and insoluble in diethyl ether, methanol, petroleum ether and water. The maximum conversions are obtained for equimolar monomer feed ratios and in bulk copolymerization.

In Figure 1 the IR spectrum of copolymer (sample 4) is presented as compared to those of homopolymers, poly-PhMI and poly-Oxz. Poly-PhMI was obtained by free-radical (AIBN) polymerization of PhMI and poly-Oxz was obtained by ring opening cationic polymerization (methyl tosylate as initiator) of Oxz. The IR spectrum of the copolymer presents absorption bands at 1700 and 1770 cm^{-1} (νC=O symmetrical and asymmetrical, respectively) corresponding the imide ring and 1625 cm^{-1} corresponding to the νC=O of the amide coming from the oxazoline ring. The IR spectra of all copolymers are basically the same,only the intensities of the bands (νC=O amide and νC=O imide) change in concordance with the copolymer composition estimated by elemental analysis.

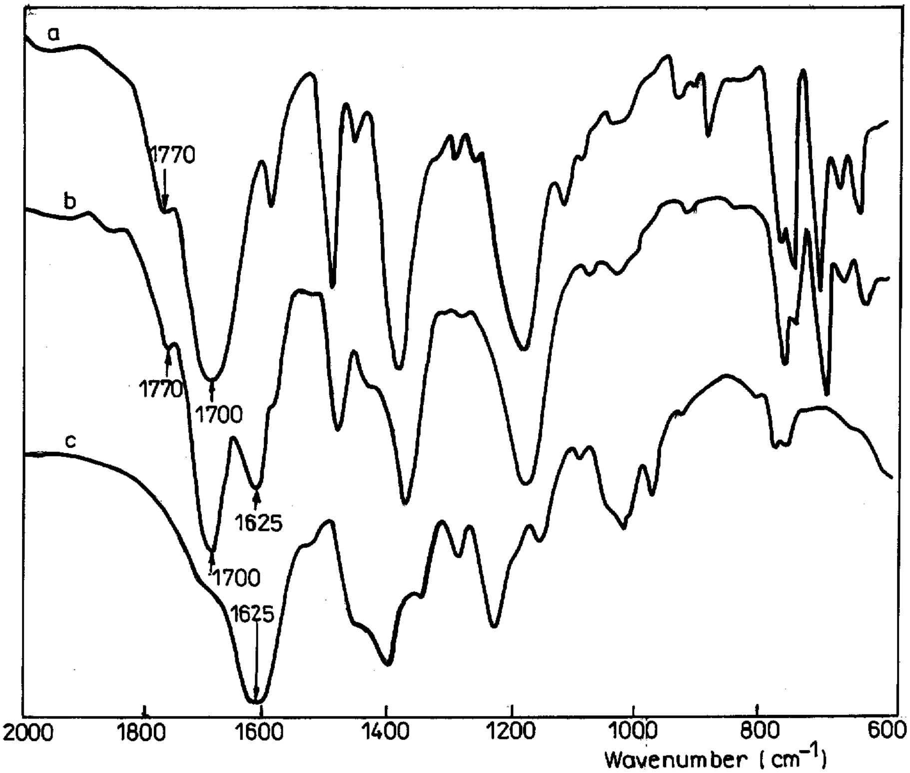
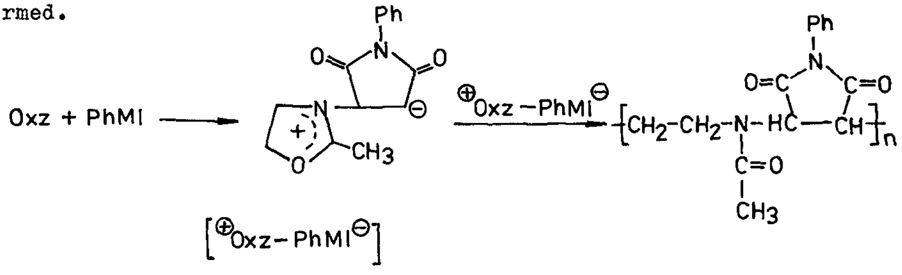


Figure 1: IR spectra (KBr pellets) of: a) poly-PhMI ,b) copolymer Oxz/PhMI (sample 4) and c)poly-Oxz

The ^{1}H-NMR spectra of the copolymers show characteristic signals due to the two structural units (Figure 2). The composition of the copolymers was estimated by comparing the integrated values for the 1-4.7 ppm range (aliphatic protons) and 6.5-8.0 ppm (aromatic protons) (see Figure 2). The same results were obtained from elemental analysis data (Table 1).

The copolymer with the highest molecular weight and aproximativelly equimolar composition was obtained by bulk copolymerization for 1:1 monomer feed ratio. In other cases the copolymers are richer in maleimide units.

The polymerization of maleimides in the presence or aromatic (pyridine) or aliphatic (triethylamine) amines was recently reported (9).Initially, the two compounds form a dipolar ion which initiates the anionic polymerization of maleimides. In our case,similarly with the reported results (1-9),a zwitterion is assumed to be formed by interaction of PhMI and Oxz. The double bond from PhMI has a low electronic density because of the presence of two electron-withdrawing C=O groups. As a result this bond is reactive and susceptible to nucleophilic attack. By addition of nucleophilic monomer (Oxz) to the double bond of PhMI a zwitterion is formed.



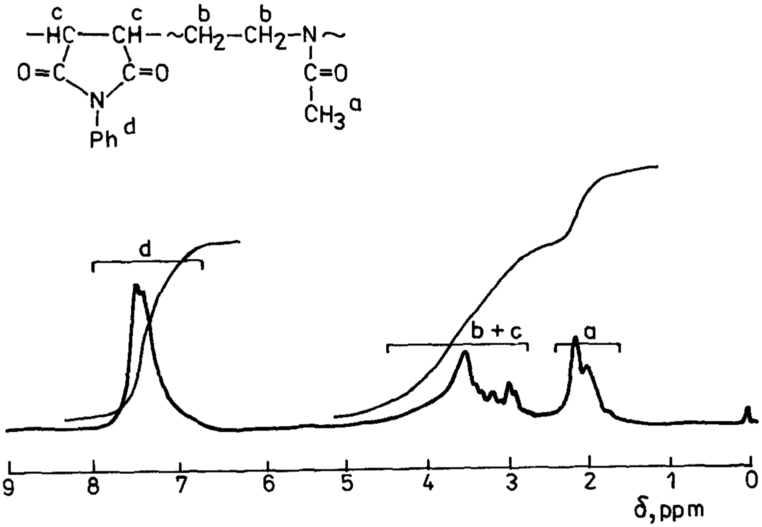
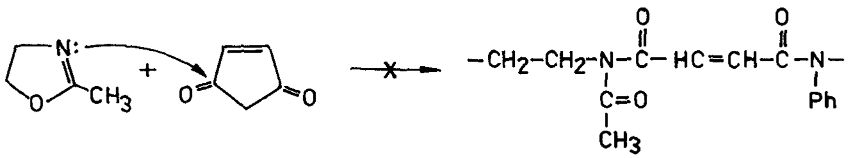


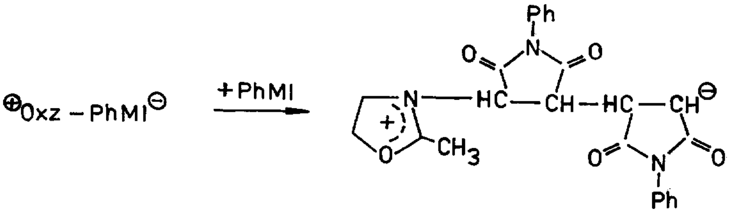
Figure 2: ^{1}H-NMR spectrum (CDCl$_3$, 55°C) of copolymer PhMI/Oxz (sample 3)

The ring opening of the imide ring by nucleophilic attack of the electron pair of nitrogen (Oxz) on the carboxilic group of the electrophilic monomer (PhMI) leading to the structure:



is not in agreement with IR and NMR data.

The propagation reaction takes place by the reaction of zwitterion with itself or by preferential attack on double bonds of PhMI.



Since the copolymers are richer in PhMI,it results that the last reaction is favourized.In fact,the tendency of the maleimide to polymerize by anionic mechanism is well known (11).

The spontaneous copolymerization of 2-methyl-2-oxazoline with other N-aryl maleimides (α-naphthyl,3-carbazolyl) takes also place. The copolymers are statistical and richer in maleimide units.

REFERENCES

1.Saegusa,T.,Angew.Chem.Int.Ed.Engl.,16,826 (1977);Makromol.Chem.Suppl., 4,73 (1981) and references therein
2.Saegusa,T.,Ikeda,H.,Fujii,H.,Pure and Appl.Chem.,50,281 (1978)
3.Balakrishnan,T.,Periyasami,M.,Makromol.Chem.,Rapid Commun.,1,307 (1980)
4.a) Saegusa,T.,Kimura,Y.,Kobayashi,S.,Macromolecules,10,236 (1977)
  b) Odian,G.,Gunatillake,P.A.,Polymer Preprints, 24(1),135 (1983)
5.Saegusa,T.,Kobayashi,S.,Kimura,Y.,Macromolecules,8,374 (1975)
6.Saegusa,T.,Kobayashi,S.,Furukawa,J.,Macromolecules,9,728 (1976)
7.Rivas,B.L.,Canessa,G.S.,Pooley,S.A.,Polym.Bull.,9,417 (1983)
8.Canessa,G.S.,Pooley,S.A.,Parra,M.,Rivas,B.L.,Polym.Bull.,10,465 (1984)
9.Ivanov,A.A.,Primel'yes,E.,Vysokomol.Soed.,A26,1300 (1984)
10.Searle,N.E.,U.S.Pat.2 444 536 (1948);Chem.Abstr.,42,7340d (1948)
11.Cubbon,R.C.P.,Polymer,6,419 (1965).

Accepted July 9, 1985

C