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Copolymers

Copolymerization Without Initiator

4. N-Acetylaziridine, 2-Methyl-2-Oxazoline with Maleic Anhydride

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SUMMARY

Copolymers of 2-methyl-2-oxazoline, N-acetylaziridine (structural isomers) and maleic anhydride were synthesized in acetonitrile in the absence of initiator. The copolymers are insoluble in solvents such as DMF, acetone, methanol, pyridine, DMSO, etc. The copolymer composition depends on the initial ratio and it was determined by elemental analysis.

INTRODUCTION

There have been reports on a new class of co and terpolymerizations in the absence of added initiator or catalyst and proceeding through zwitterion intermediate (1-9). For this type of copolymerization the combination of two comonomers is essential. One monomer must to have electrophilic reactivity ME while the other possesses nucleophilic reactivity MN. By interaction between MN and ME, an ionic species $^{+}MNME^{-}$ is generated which functions as the initiator:

$$\mathrm{MN} \quad + \quad \mathrm{ME} \quad \longrightarrow \quad \underset{1}{{}^{+}\mathrm{MNME}^{-}}$$

The genetic zwitterion 1 is responsible not only for initiation but also for the propagation reaction. The following reactions may lead to the formation of alternating copolymers.

$$1 \quad + \quad 1 \quad \longrightarrow \quad \underset{2}{{}^{+}\mathrm{MNMEMNME}^{-}}$$

$$2 \quad + \quad 1 \quad \longrightarrow \quad \underset{3}{{}^{+}\mathrm{MN(MEMN)_2ME}^{-}}$$

In general:

$$\underset{4}{{}^{+}\mathrm{MN(MEMN)_nME}^{-}} \quad + \quad 1 \quad \longrightarrow \quad \underset{5}{{}^{+}\mathrm{MN(MEMN)_{n+1}ME}^{-}}$$

We now report new copolymers prepared from 2-methyl-2-oxazoline (MOX) and N-acetylaziridine (AAz) with maleic anhydride (MA).

EXPERIMENTAL PART

Monomers: 2-methyl-2-oxazoline (MOX) (Aldrich Chem. Co.), was distilled under N_2 and the maleic anhydride (MA) (Merck), was purified by repeated sublimation (3 times). The N-acetylaziridine (AAz) was obtained by addition of aziridine (0.30 mole) to a solution of 0.30 mole acetyl chloride, 225 ml diethyl ether and triethylamine (0.30 mole). The mixture was stirred by 3 h in a water-ice bath. The N-acetylaziridine was purified by distillation (35-36 °C at 13 mmHg). The yield was 36%. The IR spectra shows an absorption band at 1660 cm^{-1} ($\nu_{C=O}$ amide) and the proton NMR ($CDCl_3$, 60MHz, TMS) shows two singlets at 2.2 ppm ($C\underline{H}_2$) and 1.5 ppm ($C\underline{H}_3$).

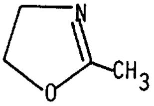
Solvent: Acetonitrile was distilled over P_2O_5 under nitrogen.

Copolymerizations: A set of 3 polymerizations were carried out keeping constant the total mole number of comonomers (MOX + MA = 0.04; AAz + MA = 0.03). In a glass tube, a mixture of MOX and MA (0.04 mole total or AAz + MA = 0.03 mole) were dissolved in CH_3CN in a thermostated bath. The copolymers were washed with diethyl ether and dried under vacuum at 40 °C.

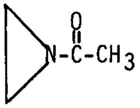
Characterization: The IR spectra (KBr) were recorded on a Perkin Elmer 577 spectrophotometer. The ^1H NMR spectrum was recorded on a Varian T60-A.

RESULTS AND DISCUSSION

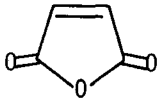
The copolymerization reactions between 2-methyl-2-oxazoline (MOX), N-acetylaziridine (AAz), as nucleophilic monomers and maleic anhydride (MA) as electrophilic monomer were carried out.



(MOX)



(AAz)



(MA)

Both copolymers, MOX/MA and AAz/MA show similar copolymerization behaviour and infrared spectra. The copolymerization reaction for AAz/MA which ones is faster than for MOX/MA. The copolymers are insoluble in water and organic solvents such as DMF, DMSO, pyridine, acetone, methanol, chloroform.

The copolymerization conditions are summarized in Table 1.

Table 1. Copolymerization MOX/MA (45 °C, CH_3CN) and AAz/MA (45 °C, CH_3CN).

Copolymer	MOX (mole)	AAz (mole)	MA (mole)	Initial Ratio	Time (h)	Yield (%)
1	0.010	-	0.030	1.0 : 3.0	115	63.3
2	0.020	-	0.020	1.0 : 1.0	115	55.9
3	0.030	-	0.010	3.0 : 1.0	115	8.0
4	-	0.010	0.020	1.0 : 2.0	18	43.7
5	-	0.015	0.015	1.0 : 1.0	18	38.5
6	-	0.020	0.010	2.0 : 1.0	18	36.6

For both copolymerization systems the yield increases as the feed monomer mixture becomes richer in maleic anhydride (Table 1, copolymer 1 and 4). The copolymerization rate for AAz/MA is faster than that for MOX/MA due to ring strain and activation of the aziridine ring.

Table 2. Elemental analysis of copolymers MOX/AM and AAz/AM.

	% C	% H	% N
Exp. Copolymer 1	49.71	4.15	4.61
Calc. $(MOX)_{1.0}\ (MA)_{2.0}\ (H_2O)_{0.5}$	49.66	4.14	4.83
Exp. Copolymer 2	52.73	4.93	7.42
Calc. $(MOX)_{1.0}\ (MA)_{1.0}$	52.46	4.92	7.65
Exp. Copolymer 3	53.99	5.82	10.64
Calc. $(MOX)_{2.0}\ (MA)_{1.0}$	53.73	5.97	10.45
Exp. Copolymer 4	51.62	5.64	6.52
Calc. $(AAz)_{1.0}\ (MA)_{1.3}\ (H_2O)_{0.25}$	50.89	4.65	6.45
Exp. Copolymer 5	52.90	5.26	7.30
Calc. $(AAz)_{1.0}\ (MA)_{1.0}$	52.46	4.92	7.65
Exp. Copolymer 6	51.73	5.73	8.32
Calc. $(AAz)_{1.3}\ (MA)_{1.0}\ (H_2O)_{0.25}$	51.80	5.33	8.54

The IR spectra of the 6 copolymers are basically the same; they did not show the $\nu_{C=O}$ of the anhydride and instead exhibit the characteristic absorption band at 1640 cm^{-1} corresponding to $\nu_{C=O}$. See Figure 1.

Since the copolymers are insoluble, copolymers compositions were determined by quantitative elemental analysis. Besides, the ratio N/C was determined, which is unaffected by the water occluded in the copolymers; these values are in agreement with the calculated values for the different copolymer compositions. See Table 3.

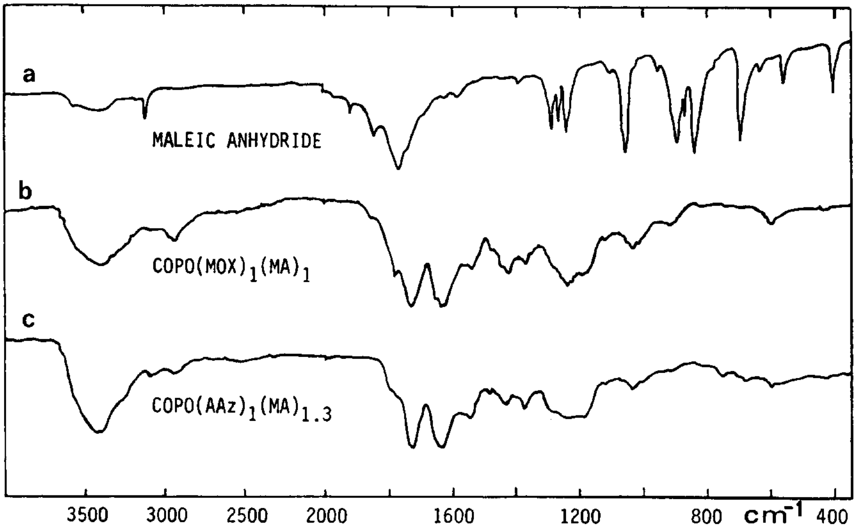


Figure 1. IR spectra (KBr) of the a) maleic anhydride, b) copolymer MOX/MA, (copolymer 2) and c) copolymer AAz/MA (copolymer 4).

Table 3. Composition of the copolymers MOX/MA and AAz/MA.

Copolymer	Monomer ratio	Copolymer* composition	N/C (theor)	N/C* (exp)
1[a]	1.0 : 3.0	1.0 : 2.0	0.097	0.093
2	1.0 : 1.0	1.0 : 1.0	0.146	0.141
3	3.0 : 1.0	2.0 : 1.0	0.194	0.197
4[b]	1.0 : 2.0	1.0 : 1.3	0.127	0.126
5	1.0 : 1.0	1.0 : 1.0	0.146	0.138
6	2.0 : 1.0	1.3 : 1.0	0.165	0.161

a) MOX/Ma ; b) AAz/MA

* Determined from the elemental analysis.

Table 3 shows that the copolymers are statistical. The copolymer composition depends on the initial composition, obtaining basically an alternating arrangement for copolymer 2 and 5. For copolymer 1 to 3 and 4 to 6 there is an equal incorporation of the comonomer that is in excess in the feed molar ratio. For copolymers 4 to 6 (AAz/MA) a lower incorporation of the maleic anhydride is observed. This behaviour is different for MOX/MA copolymers (copolymer 1 to 3) which is in agreement with the higher reactivity showed by AAz.

In relation to the copolymerization mechanism there are at least two possibilities for obtaining the initiator species. One is the addition of the nucleophilic monomer (MOX) to the double bond of maleic anhydride forming a zwitterion that contains a carbonionic group. The other is the ring opening of the maleic anhydride by nucleophilic attack of the electron pair of nitrogen (MOX) on the carboxilic group of the electrophilic monomer (MA) leading to a structure with a double bond and carboxylate anion. The IR spectrum does not show the characteristic absorption band at 1850 cm^{-1}

corresponding to the anhydride ring but show bands at 1640 cm^{-1} and 1720 cm^{-1} assignable to $\nu_{C=O}$ (ester) respectively. It is suggested that the copolymerization occurs basically by ring opening but is not possible eliminate the possibility that both routes occur simultaneously. Our interest to elucidate this problem by other techniques such as UV, ^{1}H NMR, ^{13}C NMR spectroscopies, however, could not be followed up due to the insolubility of the products.

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REFERENCES

1. Saegusa, T., Kobayashi, S., Kimura, Y., Pure and Appl. Chem. 48, 307 (1976).
2. Saegusa, T., Kimura, Y., Kobayashi, S., Macromolecules 10, 236 (1977).
3. Saegusa, T., CHEMTECH 5, 295 (1975).
4. Rivas, B., Canessa, G., Pooley, S., Polymer Bulletin 9, 417 (1983).
5. Canessa, G., Pooley, S., Parra, M., Rivas, B., Polymer Bulletin 11, 465 (1984).
6. Kobayashi, S., Isobe, M., Saegusa, T., Macromolecules 15, 703 (1982).
7. Rivas, B., Pooley, S., An. Quim. 62 (1983).
8. Saegusa, T., Kobayashi, S., Kimura, Y., Macromolecules 10, (1) 68) (1977).
9. Odian, G., Gunatillake, P.A., Macromolecules 17, (7) 1297 (1984).

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