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Copolymerization via zwitterion

13. Copolymerization of 2-ethyl-2-oxazoline with o- and p- methoxiphenylmaleimide

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SUMMARY

p-Methoxiphenylmaleimide (p-MeOPhMI) as electrophilic monomer (ME) and 2-methyl-2-oxazoline (MOX) and 2-ethyl-2-oxazoline (ETOX) as nucleophilic monomer (MN),were copolymerized in solution in the absence of initiator under different experimental conditions: (feed mole ratio, solvent, time and temperature). Copolymers were characterized by elemental analysis, IR and ^{1}H NMR spectroscopy. The copolymer composition was determined by elemental analysis and by ^{1}H NMR spectroscopy. All copolymers contain a ME:MN mole ratio greater than one.

INTRODUCTION

The process of copolymerization usually requires an initiator, radiation or catalyst, but there have been reports on a new class of copolymerizations which occur in the absence of added initiator, a "zwitterion" being the intermediate (1-12). This "non catalyst copolymerization" is based on the fact that in organic chemistry reactions between nucleophiles take place without catalyst. In this copolymerization a nucleophilic monomer (MN) reacts with an electrophilic monomer (ME) to produce a zwitterion **1** $^+$MNME$^-$ which is the key intermediate responsible for initiation as well as for propagation.

$$\mathrm{MN} + \mathrm{ME} \longrightarrow \underset{\mathbf{1}}{{}^{+}\mathrm{MNME}^{-}} \longrightarrow \underset{\mathbf{2}}{{}^{+}\mathrm{MN}(\mathrm{MEMN})_n\mathrm{ME}^{-}}$$

Previously, we have reported the copolymerization of 2-ethyl-2-oxazoline with N-phenylmaleimide (13) and with o- and p-methylphenylmaleimide (14).

This paper reports on the copolymerization of p-methoxiphenylmaleimide (p-MeOPhMI) as ME with 2-methyl-2-oxazoline (MOX) and 2-ethyl-2-oxazoline (ETOX) as MN. The copolymerizations were carried out under different experimental conditions: feed mole ratio, solvent, temperature and time.

EXPERIMENTAL

Monomers : p-methoxiphenylmaleimide (p-MeOPhMI) was synthesized according to the literature (15). 2-methyl-2-oxazoline (MOX) and 2-ethyl-2-oxazoline (Commercial reagents Aldrich Chem.Co.) were purified by distillation from KOH.

Solvents : All the solvents (acetone, benzene, acetonitrile, 2-butanone, N,N-dimethylformamide) were purified by usual methods (16).

Copolymerization : A typical procedure for the copolymerization reaction is as follows: the mixture of ETOX and p-MeOPhMI (total amount 0.014 mol) was placed in a polymerization flask under nitrogen atmosphere. The tube was kept at 70°C for 24 h. The copolymerization mixture was precipitated in diethyl ether. The copolymer was separated by centrifugation and purified by reprecipitation and dried under vacuum.

Measurements : The IR spectra were recorded on a Perkin Elmer 577 spectrophotometer. The ^{1}H NMR spectra were recorded at room temperature in a Varian T60A using $CDCl_3$ solutions. The viscosity of the copolymer was determined using DMF solvent and a Ostwald at 30.0± 0.1°C.

RESULTS AND DISCUSSION

It is known that the oxazoline derivatives homopolymerize using cationic initiator (17-19), whereas the phenylmaleimide homopolymerizes by anionic initiator (20).

In the last few years we have reported several copolymerization systems, one of them being the N-phenylmaleimide with 2-ethyl-2-oxazoline (13) and o- and p-methylphenylmaleimide with 2-ethyl-2-oxazoline (14). Simionescu and coworkers have reported the copolymerization of N-phenylmaleimide with 2-methyl-2-oxazoline (7).

We now report the copolymerization of p-methoxiphenylmaleimide (p-MeOPhMI) with 2-methyl-2-oxazoline (MOX) and 2-ethyl-2-oxazoline (ETOX).

Copolymerizations were carried out at different feed mole ratios but keeping constant the total amount of comonomers. The copolymerization conditions are summarized in Tables 1 and 2.

For equimolar feed mole ratio p-MeOPhMI/MOX, (see Table 1), the yield increases with increasing the copolymerization times (Copolymer 1-3) yielding 76% at 90 h. The same effect is observed with the temperature (Copolymer 3-5), producing the highest conversion at 70°C, determined from the insoluble fraction in diethyl ether (Copolymer 3).

Table 1.- Conditions and results of the solution copolymerization of p-methoxiphenylmaleimide (p-MeOPhMI) with 2-methyl-2-oxazoline (MOX) at different temperatures and times of copolymerization.

Copolymer	MOX (mole)	p-MeOPhMI (mole)	Time (h)	Temp. (°C)	Yield (%)	[η] (dl/g)	N/C[a] ratio	Copolymer Composition ME/MN	
								from N/C ratio	from ^{1}H NMR
1	0.010	0.010	24	70	28	0.030	0.1173	5.6 : 1.0	5.7 : 1.0
2	0.010	0.010	48	70	45	0.052	0.1253	3.1 : 1.0	3.4 : 1.0
3	0.010	0.010	90	70	76	0.085	0.1483	1.2 : 1.0	1.3 : 1.0
4	0.010	0.010	90	60	63	0.060	0.1341	2.0 : 1.0	1.9 : 1.0
5	0.010	0.010	90	50	30	0.005	0.1190	4.9 : 1.0	4.6 : 1.0
6	0.007	0.013	90	70	83	0.039	0.1416	1.5 : 1.0	1.7 : 1.0
7	0.013	0.007	90	70	43	0.014	0.1234	3.5 : 1.0	3.8 : 1.0
8	0.009	0.011	90	70	65	0.025	0.1308	2.4 : 1.0	2.6 : 1.0
9	0.010	0.010	24	60	29	0.012	0.1209	4.2 : 1.0	4.3 : 1.0
10	0.010	0.010	48	60	35	0.018	0.1312	1.8 : 1.0	2.0 : 1.0

[a] obtained from elemental analyses.

Table 2.- Conditions and results of the solution copolymerization of p-methoxiphenylmaleimide (p-MeOPhMI) with 2-ethyl-2-oxazoline (ETOX) at different temperatures and times of copolymerization.

Copolymer	ETOX (mole)	p-MeOPhMI (mole)	Time (h)	Temp. (°C)	Yield (%)	[η] (dl/g)	N/C[a)]	Copolymer Comp. ME/MN	
								from N/C ratio	from ^{1}H NMR
11	0.007	0.007	24	70	18	0.012	0.1281	2.1:1.0	2.3:1.0
12	0.007	0.007	48	70	21	0.059	0.1218	2.3:1.0	2.4:1.0
13	0.007	0.007	90	70	24	0.014	0.1221	3.0:1.0	2.8:1.0
14	0.007	0.007	90	60	20	0.009	0.1205	3.5:1.0	3.5:1.0
15	0.007	0.007	90	50	15	0.003	0.1275	2.7:1.0	2.9:1.0
16	0.005	0.009	90	70	13	0.035	0.1199	3.7:1.0	3.6:1.0
17	0.009	0.005	90	70	6	0.011	0.1305	2.0:1.0	2.2:1.0

a) obtained from elemental analyses.

Table 3.- Solvent effect on the solution copolymerization of p-methoxiphenylmaleimide (p-MeOPhMI) with 2-methyl-2-oxazoline (MOX) and 2-ethyl-2-oxazoline (ETOX) at 70°, 90 h.

Copolymer	MN (mole)	p-MeOPhMI (mole)	Solvent	Yield (%)	$[\eta]$ (dl/g)	N/C[a] ratio	Copolymer Comp. ME/MN from E.Anal.	Copolymer Comp. ME/MN from ^{1}H NMR
18	0.010	0.010	CH_3CN	76	0.085	0.1483	1.2 : 1.0	1.3 : 1.0
19	0.010	0.010	$CH_3CH_2COCH_3$	57	0.050	0.1152	7.0 : 1.0	7.0 : 1.0
20	0.010	0.010	C_6H_6	53	0.051	0.1219	3.9 : 1.0	3.6 : 1.0
21	0.007	0.007	CH_3CN	24	0.014	0.1221	3.0 : 1.0	2.8 : 1.0
22	0.007	0.007	$CH_3CH_2COCH_3$	36	0.003	0.1271	3.0 : 1.0	3.3 : 1.0
23	0.007	0.007	C_6H_6	11	0.049	0.1257	2.5 : 1.0	2.8 : 1.0

[a] obtained from elemental analyses.

Subsequently solution copolymerization at different feed mole ratios by keeping constant the temperature (70°C) and time (90 h) were carried out (Copolymers 3,6-8). Yield increases with increasing the p-MeOPhMI in the feed mole ratio 43, 65, 76 and 83% respectively. The intrinsic viscosity behaves similarly.

For the solution copolymerizations p-MeOPhMI/ETOX (seeTable 2), the yield is lower than for p-MeOPhMI/MOX systems due to the steric hindrance of the ethyl group compared to the methyl group. But the effect of the time and the copolymerization temperature is the same that observed for the anterior copolymerization systems. For the p-MeOPhMI/MOX system the more polar solvent acetonitrile produces a copolymer with the highest yield (76%), intrinsic viscosity (0.085 dl/g) (see Table 3).

The conversions for the three copolymers p-MeOPhMI/MOX are higher than the copolymers p-MeOPhMI/ETOX.

All copolymers were characterized by elemental analyses, IR and ^{1}H NMR spectroscopy.

The IR spectra of all the copolymers show similar absorption bands at 1625 cm^{-1} corresponding to $\nu_{C=O}$ (amide) attributed to the openning of oxazoline ring and at 1700 cm^{-1} corresponding to $\nu_{C=O}$ anhydride. (see Fig. 1).

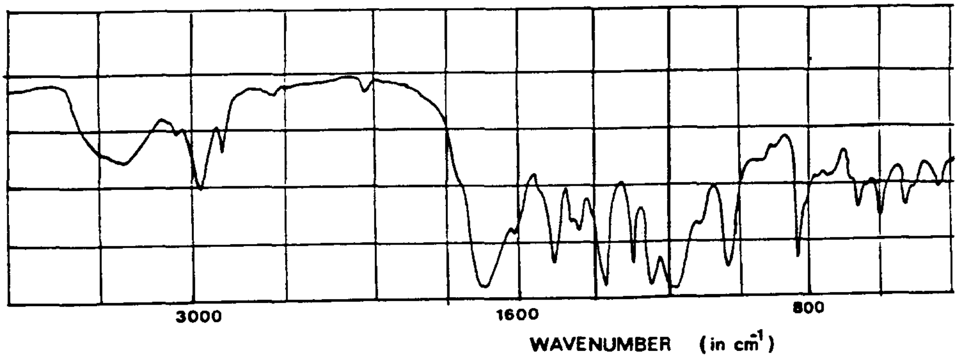

Fig. 1 IR spectrum (KBr) of copolymer sample 3 p-MeOPhMI/MOX

All the ^{1}H NMR spectra show the absorption signals expected. The copolymers p-MeOPhMI/MOX show the following signals: signal (a) at δ=1.8-2.2 attributed to -CH$_3$ protons from MOX; broad signal (b) at δ=2.6-4.4ppm assigned to -CH$_2$-N-CH$_2$; -CH-CH; -OCH$_3$- protons and signal (c) at δ=6.8-7.5 corresponding to aromatic protons.

The copolymers p-MeOPhMI/ETOX show the following signals: signal (a) at δ=0.9-1.4 assigned to -CH$_2$CH$_3$- protons from ETOX; signal (b) at δ=2.1-2.6 assigned to -CH$_2$CH$_3$ protons a broad signal (c) at δ=2.7-4.4 attributed to -CH$_2$-N-CH$_2$-; -CH$_3$-$\underline{CH}_2$-CO and OCH$_3$ protons and signal (d) at δ=6.6-7.5 attributed to aromatic protons (see Fig. 2).

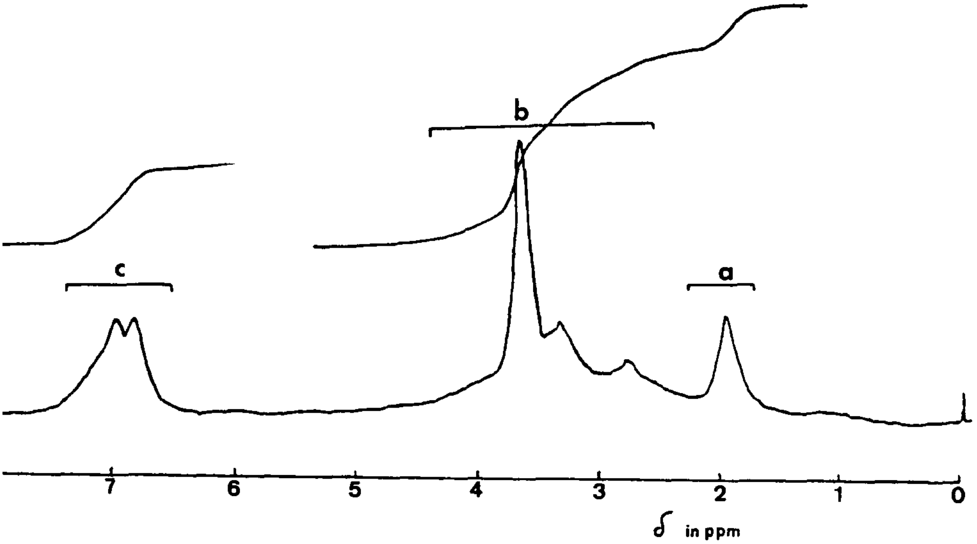

Fig. 2.- ^{1}H NMR spectrum of p-MeOPhMI/MOX copolymer sample 3 (60MHz, $CDCl_3$, room temperature, internal standard: TMS).

The copolymer composition was determined by comparing the equivalent proton area of the ME and MN units incorporated into the copolymer (see Tables 1-3). The proton area of the ME unit was determined from the aromatic protons which resonate between δ=6.6-7.5 ppm and for the MN unit was determined from the methyl protons which resonate between δ=1.8-2.2 ppm for MOX and δ=0.9-1.4 ppm for ETOX.

All the copolymers are statistical and rich in ME, due to the greater reactivity of p-MeOPhMI to homopolymerizes in respect to the copolymerization reaction with the nucleophilic comonomers. For copolymers p-MeOPhMI/MOX, the temperature and time of copolymerization affect copolymer composition. Increasing the temperature decreases the homopropagation reaction of p-MeOPhMI, yielding at 70°C a copolymer 1.2:1.0(See Table 1, copolymer 3). Similar effect is observed with the copolymerization time, but in this case as the reactivity of p-MeOPhMI is greater that of oxazoline derivatives, the homopropagation is favoured in respect to the copolymerization reaction. After 24 h it is possible to observe this effect by producing a copolymer richer in p-MeOPhMI.

Subsequently at 48 and particularly at 90 h, as p-MeOPhMI, was more quickly consumed through homo and copolymerization reactions than MN, at the long period of reaction the unreacted MN may react with the comonomer ME and also with other molecules of MN, producing a copolymer with a composition near to 1:1.

The copolymer is not alternating $\left(MN-ME \right)_n$ and the "copolymer composition" is almost 1.0:1.0 at 90 h and 70°C (see Table 1, copolymer 3).

Unfortunately, we do not have higher resolution ^{1}H NMR equipment to study the presence or absence of blocks of boths monomers.

In respect to the copolymerization mechanism, the statistical copolymers which are richer in p-MeOPhMI, arise by propagation due to preferential attack on the double bond of p-MeOPhMI.

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REFERENCES

1. T.Saegusa, CHEMTECH 5, 295 (1975)
2. T.Saegusa, S.Kobayashi, Y.Kimura, Macromolecules 7, 256 (1974)
3. T.Balakrishnan, M.Periyasami, Makromol.Chem.Rapid.Commun. 1, 307 (1980).
4. G.Odian, P.A.Gunatillake, Macromolecules 17, 297 (1984)
5. G.Odian, P.A.Gunatillake, D.Tomalia, Macromolecules 18, 605 (1985)
6. P.A.Gunatillake, G.Odian, D.A.Tomalia, Macromolecules 21, 1556 (1988)
7. C.I. Simionescu, M.Grigoras, E.Bicu, G.Onofrei, Polym.Bull.(Berlin) 14, 79 (1985)
8. B.L.Rivas, S.A.Pooley, An.Quím. Ser C: 79, 62 (1983)
9. B.L.Rivas, G.S.Canessa, S.A.Pooley, H.A.Maturana, U.Angne, Eur.Polym. J. 21, 939 (1985).
10. B.L.Rivas, G.S.Canessa, S.A.Pooley, Makromol.Chem. 187, 71 (1986)
11. B.L.Rivas, G.S.Canessa, S.A.Pooley, Makromol.Chem. 188, 149 (1987)
12. B.L.Rivas, G.S.Canessa, S.A.Pooley, Makromol.Chem.Rapid.Commun. 8, 364 (1987).
13. B.L.Rivas, G. del C. Pizarro, G.S.Canessa, Polym.Bull. (Berlin) 19 123 (1988).
14. B.L.Rivas, G. del C. Pizarro, Eur.Polym.J. (In press)
15. M.Cava, H.Deano, K.Muth, Org.Synth. 41, 93 (1961)
16. "Organikum" VEB Deutscher Verlag der Wissenschaften Berlin, 1972.
17. B.L.Rivas, S.I.Ananías, Polym.Bull. (Berlin), 18, 189 (1987)
18. J.Bartulín, B.L.Rivas, M.Rodríguez, U.Angne, Makromol.Chem 183 , 2935 (1982).
19. T.Saegusa, H.Ikeda, H.Fujii, Macromolecules 5, 108 (1972).
20. R.C.E.Cubbon, Polymer 6, 419 (1965).

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