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Polymerization of methyl and phenyl oxazoline initiated with carboxylic acid chlorides

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Summary

Methyl and phenyl oxazoline were polymerized using carboxylic acid chlorides as initiators. The first step of the reaction was shown to consist in a fast reaction of the carboxylic acid chloride with the oxazoline. Resulting product, which was isolated and identified, act as the proper initiator of the polymerization of the oxazoline, which proceeds via covalent or, when chloride counter ion is replaced with iodide or triflate, ionic active species. Apparent rate constants of the chain growth were determined. When methacryloyl chloride is used as initiator macromonomers are obtained, which were copolymerized with styrene. Macromolecular carboxylic acid chlorides initiate the polymerization of oxazolines, yielding graft polymers.

Introduction

Polymerization of 2-oxazolines remains subject of significant importance, also because it allows to obtain polymers of variable properties, which may easily be controlled (for review, see (1)). The search for new initiators is one of the subjects; Lewis acids, protonic acids and their esters, alkyl halogenides being most frequently used. It has been shown that acylating agents - the chloroformates are efficient initiators of the polymerization of 2-oxazolines (2) and open some new synthetic possibilities (3,4). In view of these findings it was decided to investigate the possibility to initiate the polymerization of these monomers by carboxylic acid chlorides, the mechanism of this reaction and its applicability to polymer synthesis.

Experimental

Monomers

Methyl oxazoline (Aldrich) was distilled over KOH prior to use. Phenyl oxazoline was synthesized from aminoethanol and benzonitrile as described in (5). Styrene was distilled prior to use.

Initiators

Methacryloyl chloride was synthesized from methacrylic acid and PCl_5. Acetyl chloride was distilled prior to use. Silver triflate (Aldrich) and KI (Aldrich) were dried i.v. prior to use.

Solvents were purified in usual way.

Polymerizations:

Monomer (methyl or phenyl oxazoline) was dissolved in acetonitrile or nitrobenzene (2.0 mol/l) and the proper amount of the initiator (acetyl chloride or methacryloyl chloride) were added under stirring. In experiments where chloride counter ion was exchanged the exchanging agent (KI or silver trifluoromethanesulphonate) was added under stirring (KI - twice the molar amount of the initiator, silver triflate 10% excess). The stirred reaction mixture was placed in thermostated bath. Progress of the reaction was checked by gas chromatography.

The copolymerization of the macromonomer with styrene was carried out in bulk at 80°C using AIBN as initiator.

Poly(styrene-co-methacryloyl chloride) was obtained in an AIBN intiated polymerization in bulk at 90°C.

Phenyl oxazoline was grafted onto so obtained copolymers in nitrobenzene solution at 90oC. 1.04 g polymer was dissolved in 16.5 mL dry nitrobenzene, KI (10% excess over the carboxylic acid chloride units) and 1.3 mL phenyl oxazoline were added under stirring. The progress of the reaction was followed by gas chromatography and polymer samples taken at the chosen intervalls of conversion. The polymers were precipitated twice from methylene chloride into hexane.

Reaction of acetyl chloride with phenyl oxazoline

Phenyl oxazoline (1 g, 0.007 mol) was added to a solution containing equimolar amount of acetyl chloride in 10 ml dry benzene under cooling with ice. The reaction was allowed to completed overnight at room temperature. Benzene was evaporated i.v. and the oily residuum dried i.v. at 50°C. 1H NMR ($CDCl_3$): 1.97 ppm (s, 3H, CH_3), 3.59 ppm (t, 2H, CH_2-N), 3.97 ppm (t, 2H, CH_2-Cl), 7.28 ppm - 7.75 ppm (5H, m, C_6H_5). Molecular mass: calculated 225, found from vapor pressure osmometry 211.

Elemental analysis: calculated for $C_{11}H_{12}O_2NCl$ C = 58.54%, H = 5.36%, O = 14.18%, N = 6.20%, Cl = 15.71%, found C = 58.1%, H = 5.2%, N = 6.4%, Cl = 14.3%

Hydrolysis of the poly(phenyl oxazoline) obtained using methacryloyl chloride

0.5 g of the polymer ($M_n = 992$) were refluxed for 8 hrs in 5% aqueous HCl. The precipitated benzoic acid was filtered off and the filtrate extracted with chloroform. Methacrylic acid was detected in the extract using gas chromatography (DB-Wax columns).

Polymer characterization

Molecular weights were determined by vapor pressure osmometry in $CHCl_3$ (polymers of methyl oxazoline, insoluble in THF) or GPC in THF using Eurogel 100, 1000 and 10000 5μm columns.

NMR spectra were measured at 300 MHz or 80 MHz.

Results and discussion

Acetyl chloride initiates the polymerization of both methyl and phenyl oxazoline. At the chosen conditions (see fig. 1a) the conversion of the more basic methyl oxazoline is completed within 50 hrs.

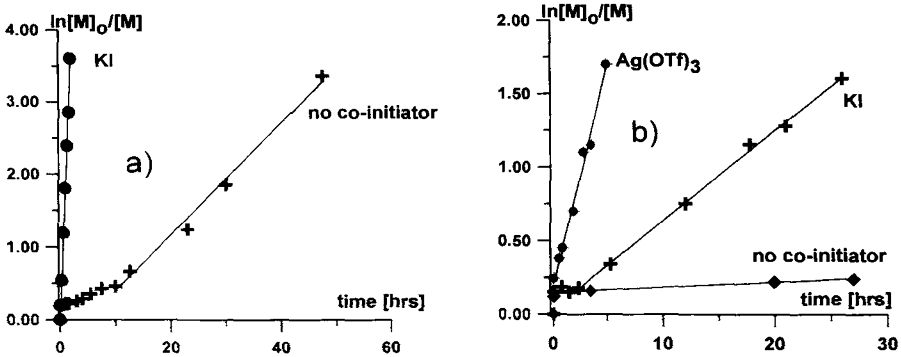


Fig. 1 Polymerization of methyl oxazoline (a) and phenyl oxazoline (b) initiated with acetyl chloride. Solvent: acetonitrile, $[M]_0 = 2.0$ mol/L, $[I]_0 = 0.2$ mol/L, temp. 80°C

Table 1. Polymerization of methyl oxazoline and phenyl oxazoline initiated with acetyl chloride
solvent: acetonitrile (methyl oxazoline) or nitrobenzene (phenyl oxazoline), $[M]_0 = 2$ mol/L

Monomer	$[M]_0/[I]_0$	M_n		
		calc. from feed	VPO (a) or GPC (b)	NMR
methyl oxazoline	3	298	330 (a)	-
methyl oxazoline	5	468	410 (a)	-
methyl oxazoline	15	1318	1410 (a)	-
phenyl oxazoline	3	420	483 (b)	480
phenyl oxazoline	10	1513	1610 (b)	1410
phenyl oxazoline	60	8863	9600 (b)	-

The less reactive phenyl oxazoline requires more drastic conditions, it proceeds within 35 hrs in nitrobenzene at 130°C.

Chloride counter ion is known to cause the polymerization of 2-oxazolines to proceed via covalent active centers with low reaction rates. When it is replaced with triflate counter ion by the action of silver triflate or iodide counter ion by the addition of KI, the reaction becomes faster by more then two orders of magnitude. When the counter ion is exchanged, even phenyl oxazoline may be polymerized to almost full conversion in acetonitrile at 80°C within 30 hrs (fig. 1a,b).

Counter ion exchange using silver salts cannot be effected in the polymerization of methyl oxazoline, as the silver cations are complexed by both the monomer and the polymer,

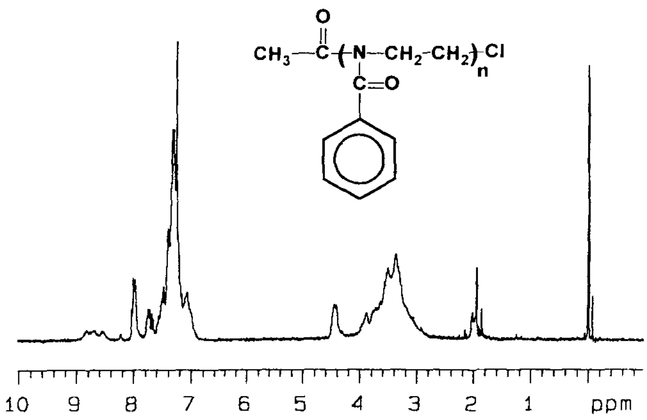


Fig. 2. 1H NMR spectrum of poly(phenyl oxazoline) obtained using acetyl chloride as initiator ($CDCl_3$, 300 MHz)

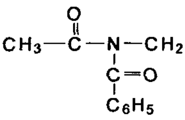
making the precipitation of silver chloride and an efficient exchange of the counter ion impossible.

The initiator is being incorporated quantitatively into polymer chain, as indicated by the comparison of the M_n values determined by VPO with values obtained from 1H NMR (fig. 2, table 1) by comparing the intensities of the signal of the CH_3 group from the initiator with the signals of the polyoxazoline moieties. Polymers of M_n up to 10000 are obtained. Where measured (polymers of phenyl oxazoline) the molecular mass distribution is rather broad, varying between 1.2 to 1.5.

The time - conversion plots of the polymerization course (fig. 1) establish that in the first step of the reaction an amount of the oxazoline equimolar with the amount of the added initiator is consumed almost instantaneously. Simultaneously, the initiator is consumed and cannot be detected by the gas chromatography. Only later the comparatively slow polymerization proceeds. This indicates that the first step of the reaction consists in a fast reaction of the carboxylic acid chloride with the oxazoline.

To confirm this phenyl oxazoline was reacted with an equimolar amount of acetyl chloride. The product was isolated and identified to (I) by 1H NMR, elemental analysis and molecular weight measurement.

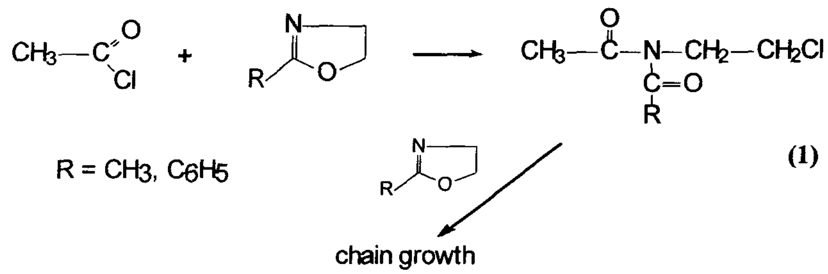
This compound was first obtained and identified by Nehring and Seeliger (6).



$$CH_3-\overset{O}{\overset{\|}{C}}-\underset{\underset{C_6H_5}{|}}{\underset{C=O}{\underset{|}{N}}}-CH_2-CH_2Cl$$

(I)

The above findings allow to establish the reaction route shown in scheme (1).



(1)

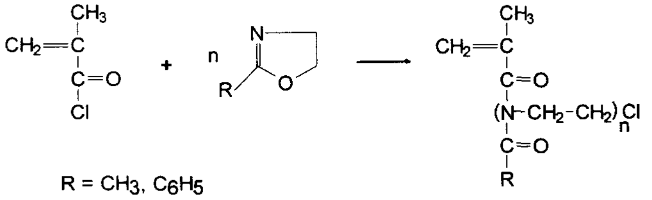
The nature of the active species in the chain growth depends upon the nature of the substituent R and upon the counterion: covalent species dominate with Cl^- as counterion, is Cl^- replaced with I^- or tosylate anion the growth occurs via oxazolinium cations.

Table 2. Apparent rate constants (L/mol.s) of the chain growth in the polymerization of methyl and phenyl oxazoline initiated with acetyl chloride (acetonitrile, 80°C, *) - nitrobenzene, 140°C)

	Initiator		
Monomer	CH_3COCl	CH_3COCl + KI	CH_3COCl + AgOTf
Methyl oxazoline	$5.4 \cdot 10^{-5}$	$2.0 \cdot 10^{-4}$	-
Phenyl oxazoline	$8.0 \cdot 10^{-6}$*)	$6.1 \cdot 10^{-4}$	$3.3 \cdot 10^{-3}$

Apparent rate constants of the chain growth have been determined from the linear part of the time - conversion plot (table 2). They are in the same order of magnitude as known for other initiating system of the polymerization of oxazolines (7,8).

Also methacryloyl chloride may be used to initiate the polymerization of phenyl and methyl oxazoline (scheme (2), yielding polyoxazoline chains containing acrylic double bond.



(2)

The structure was proven by 1H NMR spectroscopy (fig. 3). To further evidence the presence of the methacrylic group the obtained macromonomer was hydrolyzed using aqueous HCl. It is known that under such conditions the amide bonds are broken and the poly(phenyl oxazoline) is converted into poly(ethylene imine) (9) and methacrylic amide to methacrylic acid. Methacrylic acid was detected and identified in the chloroform extract of the reaction mixture using gas chromatography.

The macromonomer of phenyl oxazoline with the degree of polymerization DP = 6 as determined from 1H NMR was copolymerized with styrene in bulk at the molar ratio of oxazoline units to styrene varying from 1 : 1 to 1 : 4. In no case complete conversion of the macromonomer was achieved. The crude product was extracted with methanol to remove the unreacted macromonomer. The methanol insoluble part was examined by 1H NMR and GPC. From NMR measurements it was determined that at most ca. 40% of the macromonomer was incorporated into the polystyrene chains. The resulting copolymers showed a rather broad molecular weight distribution with M_n varying from 65000 to 20000 and M_w/M_n from 6 to 4.

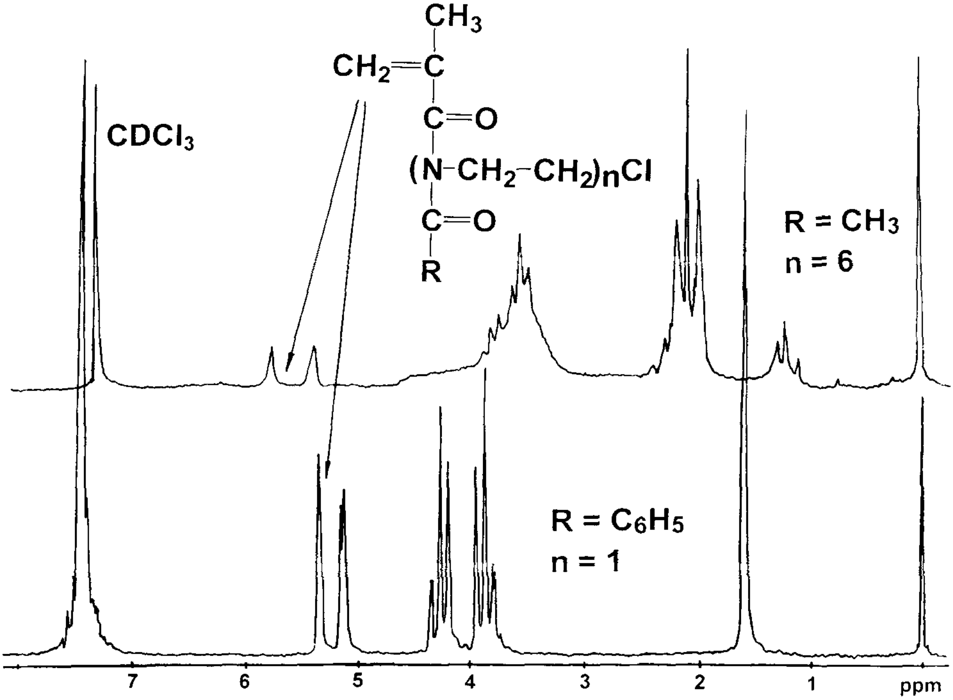
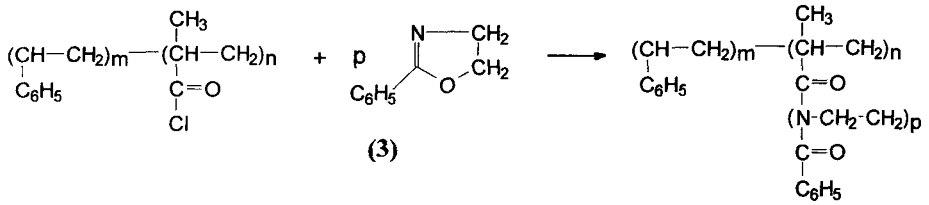


Fig. 3. 1H NMR spectra of poly(methyl oxazoline) (a) and poly(phenyl oxazoline) (b) obtained using methacryloyl chloride as initiator ($CDCl_3$, 80 MHz)

To demonstrate the possibility to apply the macromolecular carboxylic acid chlorides for the synthesis of graft copolymers the copolymer of styrene and methacryloyl chloride containing 17 mole% of acid chloride units was synthesized and used to initiate the copolymerization of phenyl oxazoline (scheme 3, table 3).



(3)

Polymers with the number average length of oxazoline side chains from 2 to 5 were obtained, as determined from 1H NMR.

Table 3. Grafting of phenyl oxazoline onto poly(styrene-co-methacryloyl chloride) containing 17 mole% of acid chloride units. Initial molar ratio of acid chloride units to phenyl oxazoline 1 : 6 (nitrobenzene, 90°C)

Time [h]	Conversion [%]	Average length of grafted oxazoline chains		GPC	
		calc. from feed and conv.	det. from 1H NMR	M_n	M_w/M_n
0	0	0	0	30100	3.10
3	20	1.20	1.22	19500	2.21
9	31	1.86	1.82	12400	1.84
14	37	2.22	2.17	12100	1.61
32	81	4.86	4.91	16700	2.23

Noteworthy is the significant difference in the properties of the graft copolymers so obtained and the copolymers of styrene and phenyl oxazoline macromonomers described above. Although both main chains are similar, the graft copolymers show clearly that the phenyl oxazoline side chains change the hydrodynamic properties of the polystyrene chains, causing a decrease in the elution volume in the GPC and simulating an apparent decrease in the molecular mass and an apparent narrowing of its distribution.

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