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 PC15. 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 initiated polymerization in bulk at 90°C.

Phenyl oxazoline was grafted onto so obtained copolymers in nitrobenzene solution at 90°C. 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 intervals 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 (CDCl3): 1.97 ppm (s, 3H, CH3), 3.59 ppm (t, 2H, CH2-N), 3.97 ppm (t, 2H, CH2-Cl), 7.28 ppm - 7.75 ppm (5H, m, C6H5). Molecular mass: calculated 225, found from vapor pressure osmometry 211.

Elemental analysis: calculated for C11H12O2NCl 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 (Mn = 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 CHCl3 (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.