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Copolymerisation of ε-caprolactone and trimethylene carbonate catalysed by methanesulfonic acid

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ABSTRACT

The copolymerisation of ε-caprolactone (ε-CL) and trimethylene carbonate (TMC) catalysed by methanesulfonic acid was investigated. Preliminary copolymerisation tests using a monofunctional initiator confirm that the side bidirectional propagation previously detected in the homopolymerisation of TMC is also present in the copolymerisation. The comonomers in the ε-CL/TMC system do not follow first order kinetics. The values of the reactivity ratios obtained by the Kellen–Tüdös method ($r_{\varepsilon\text{-CL}} = 2.90$; $r_{TMC} = 0.62$) suggest that random copolymerisation can be achieved, although the copolymer will be richer in ε-CL. Dihydroxyl-telechelic ε-CL/ TMC random copolymers were prepared using a bifunctional initiator. ^{1}H and ^{13}C NMR, SEC and DSC measurements show that the poly(TMC-*co*-ε-CL) samples presented the expected microstructural characteristics, a unimodal molar-mass distribution and a very narrow polydispersity. Based on these features a novel route for the preparation of block copolyesters with tuned properties, and highly regarded in the development of materials for biomedicine, may be foreseen.

1. Introduction

Synthetic aliphatic polyesters like poly(ε-caprolactone), polylactide, polyglycolide (PCL, PLA, PGA) and related copolymers are highly regarded in the development of materials for biomedicine [1–3]. Aliphatic polycarbonates like poly(trimethylene carbonate) (PTMC), on the other hand, are not as attractive for biomedical applications, not only due to their weak mechanical properties, but also due to their higher stability in physiological conditions, strong hydrophobicity and lack of functionality, which reduces their biological compatibility [4,5]. PTMC and related copolymers found their place in the field of biomaterials as components of block copolymers and in blends with brittle PLA, PCL or polyhydroxybutyrate (PHB) [5,6]. The copolymerisation of trimethylene carbonate with cyclic esters offers a strategy to tune both the physicochemical properties and the degradation behaviour of the resulting materials.

Cationic homo and copolymerisation of ε-caprolactone and lactide monomers initiated by an alcohol and catalysed by trifluoromethanesulfonic acid (HOTf) or methanesulfonic acid (MSA), proceed by an activated monomer (AM) mechanism in a controlled/living manner, without detectable side processes [7–14].

The use of these acid catalysts is very interesting from the viewpoint of operational simplicity and environmental compatibility, particularly for MSA. Nevertheless, performing the controlled polymerisation of TMC using such catalysts is rather problematic. This occurs because, in addition to the main AM mechanism, where the monomer activated by the acid catalyst will undergo nucleophilic attack at the

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carbonyl carbon atom by the initiating or propagating alcohol (Scheme 1), there is a side process that reduces the average molar mass (as more than one chain of polymer per initiator molecule is formed) and broadens the molar mass distribution of the main process (Scheme 2) [15,16].

This side process was first proposed as resulting from ACE initiation (where the monomer activated by the acid catalyst would ring-open, due to the nucleophilic attack of another non-activated monomer molecule) followed by spontaneous decarboxylation and subsequent combined (AM/ACE) bidirectional propagation, occurring respectively at the hydroxyl and oxonium terminal chain moieties, step (i) of Scheme 2. We recall here that ACE propagation consists in a nucleophilic attack of an oxygen atom from the monomer on the α-carbon atom in tertiary oxonium ion located at the growing chain end, whereas AM propagation involves a nucleophilic attack of an oxygen atom from the chain terminal OH group on the activated monomer moiety. By keeping a low concentration of TMC in the reactor (using multifeed/continuous feed approaches), the active chain end initiation step (i) in Scheme 2 can be suppressed, allowing polymerisation control [15].

Very recently, it was shown that the combined (AM/ACE) bidirectional propagation shifts to a bidirectional AM propagation (probably as consequence of an intermediate proton shifting, step (ii) in Scheme 2), and globally the propagation of this side process behaves as a bidirectional AM propagation. Accordingly, PTMC formed in the presence of a monofunctional initiator, shows a bimodal molar mass distribution and the polymer generated by side bidirectional AM propagation always presented twice the molar mass of polymer originated from the main unidirectional AM propagation. It was also demonstrated that the use of a bifunctional alcohol (leading to a situation where all chain propagations are bidirectional) enables the preparation of PTMC presenting unimodal molar-mass distribution and very narrow polydispersity, offering an alternative way to prepare PTMC with a better controlled chain population [16].

This study aims to find if the proposed bifunctional initiator approach can be successful for the preparation of hydroxyl telechelic random poly(TMC-co-ε-CL) with unimodal molar mass distribution using the environmentally friendly MSA catalyst. For this purpose, it was checked in a preliminary study, if the proposed mechanistic pathways developed for MSA-catalysed homopolymerisation of TMC still apply in the case of copolymerisation with ε-caprolactone, and the reactivity ratios for the two monomers were determined, foreseeing the possibility to prepare random copolymers. Next, several copolymerisations of ε-CL and TMC were performed with 1,4-phenylenedimethanol (PDM) as bifunctional initiator and the structure of the copolymers obtained was investigated by ^{1}H and ^{13}C NMR, SEC and DSC.

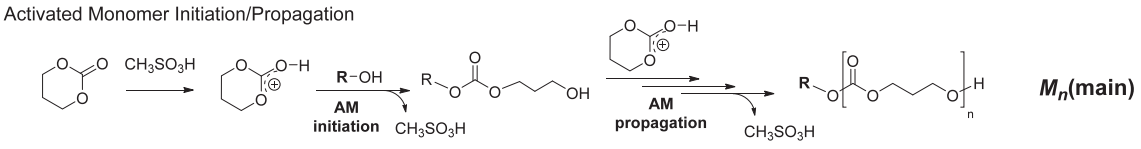
2. Experimental

2.1. Materials

All reactions and manipulations were performed under an inert atmosphere of argon, using standard Schlenk techniques. Commercial toluene (XiLab, 99%) and THF (JT Baker, 99%) were first refluxed and distilled from CaH_2 prior to use. Toluene was dried over polystyryl lithium and cryodistilled. THF was dried over metallic sodium/benzophenone and cryodistilled. Trimethylene carbonate (TMC, kindly donated by Boehringer) was dissolved in dry THF (0.7 g/mL) and stirred over CaH_2 for 3 days, filtered, recrystallized twice from cold dry THF and finally dried under vacuum and stored at −20 °C in a flask under argon. Fresh ε-caprolactone (ε-CL, Alfa Aesar, 99%) was stirred with CaH_2 for two days, purified by fractionated distillation at reduced pressure and stored under argon. Biphenyl-4-methanol (BPM, Alfa Aesar, 98%) was recrystallized from dichloromethane and 1,4-phenylenedimethanol (PDM, Roth, 99%) was used as received. The internal standard used for ^{1}H NMR, 1,2-diphenylethane (DPE) was recrystallized from petroleum ether, dried under vacuum and stored in a flask under argon. Methanesulfonic acid (MSA, Aldrich, 99.5%) was bubbled for some hours with argon, prior to use, then stored in a flask under this gas. *N,N*-diisopropylethylamine (DIPEA, Aldrich, 99%) was used as received.

2.2. Polymerisation procedure

Preliminary ε-CL/TMC copolymerisations were performed in order to investigate the mechanistic features and calculate the reactivity ratios. Monomer feed ratios of 1:4, 1:1 and 4:1 were used, keeping the total initial monomer concentration $[\varepsilon\text{-CL}]_0 + [\text{TMC}]_0$ at 1 M. For the test with $[\varepsilon\text{-CL}]_0 = [\text{TMC}]_0$, trimethylene carbonate (1.1 g, 10.8 mmol), the monofunctional initiator biphenyl-4-methanol (22.0 mg, 0.117 mmol, 0.117 mmol OH, ~0.005 equivalents of total monomer) and the NMR internal standard 1,2-diphenylethane (200 mg, 1.1 mmol, ~0.05 equivalents of total monomer) were introduced under argon in a 100 ml round-bottom flask. ε-CL (1.2 mL, 10.8 mmol) and dry toluene (20 mL) were added, under argon, from burettes. The flask was placed in an oil bath set to 30 °C and



Scheme 1. The Activated Momoner (AM) mechanism in the particular case of the ring-opening polymerisation of TMC catalysed by methanesulfonic acid (counter-anion omitted for clarity).