

Synthesis of functionalized polylactide by cationic activated monomer polymerization

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ABSTRACT

Functionalized polylactides (PLAs) containing acryloyl, methacryloyl or propargyl end groups have been obtained by cationic ring-opening polymerization performed in the presence of appropriate alcohols (HEMA, HEA, propargyl alcohol) as initiators and triflic acid as a catalyst. ¹H NMR, MALDI TOF and GPC analysis indicated almost quantitative initiation and confirmed the expected structure and molecular masses of the obtained PLAs. The conditions were found in which transesterification process (usually accompanying the cyclic esters propagation) can be avoided. PLAs functionalized with double bond were successfully homopolymerized and copolymerized with butyl acrylate in the presence of AIBN. PLA with triple bond at one chain end was effectively coupled with a model azide by 1,3-dipolar Huisgen cycloaddition ("click" reaction) in order to prove its ability to be further functionalized.

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1. Introduction

There is a continuous and still increasing interest in aliphatic polyesters due to the fact that at least some of the polymers belonging to this class are biodegradable and may be obtained from renewable resources. Polylactide, an aliphatic polyester and biocompatible thermoplastic, is currently the most promising polymeric material considered for controlled drug release, implantable composites, bone fixation parts, packaging and paper coatings, sustained release systems for pesticides and fertilizers, compost bags, etc.

Properties of polylactide, especially the rate of degradation, may be altered by copolymerization of lactide with other lactones [1–3]. Among those systems, copolymers of lactide and ϵ -caprolactone have been studied most extensively [4–9]. Random as well as block or graft copolymers have been studied.

Thus, there is an interest in developing convenient synthetic procedures for the synthesis of lactide polymers containing at one or both ends reactive groups that may be used as precursors of segments in block copolymers or side chains in graft copolymers.

Functional groups can be introduced at the end of a polylactide molecule by applying two different strategies: functionalization of a preformed polymer or introducing the initiator fragment containing a reactive group in the initiation step. The latter method, leading to polymers containing one reactive group as a head group, is often preferred because by a reaction of end groups of a

preformed polymer it is frequently difficult to attain quantitative functionalization while by introducing a functional group into the initiator molecule, high (often almost 100%) functionalization efficiency may be achieved. Both approaches were used for the synthesis of macromonomers based on polylactide [10–16], although incorporation of functional groups through the initiation can be applied only to polymers obtained by ring opening polymerization (polyesters may be synthesized also by polycondensation).

End-functionalized hydroxyethyl methacrylate macromonomers of poly(L-lactide) (HEMA–PLA) were synthesized using hydroxyethyl methacrylate/aluminum alkoxides (mono- and tri-) as initiators [9,10]. Polylactide with predictable molecular weight (about 2000) and narrow molecular weight distribution ($M_w/M_n \sim 1.2$) was obtained. By reaction of aluminum alkoxide end group with methacryloyl chloride, Jerome and Teyssie obtained α,ω -macromonomers. These macromonomers were successfully copolymerized with 2-hydroxyethyl methacrylate in the presence of AIBN as a radical initiator, giving biodegradable amphiphilic networks [10]. Monofunctional polylactide macromonomers were obtained by coordination polymerization of lactide performed with HEMA as an initiator in the presence of tin octoate as a catalyst [12]. Macromonomers with molecular weights ranging from 1400 to 19,000 were characterized by FT-IR, NMR, GPC, DSC, WAXS and CD. Macromonomer with HEMA moiety, synthesized by another group, was used for copolymerization with TEMPO-substituted acrylamide in order to synthesize electroactive copolymers [13]. Tin octoate catalyst was also used for the synthesis of poly-D,L-lactide macromonomers using HEA as an initiator [14]. After conversion of acrylate end group into alkoxyamine group, PLA with M_n

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about 10,000 was used as a macroinitiator in nitroxide-mediated polymerization of HEA and HEMA. Another catalyst for the synthesis of polylactide with methacrylate end group was used by Hadjichristidis et al. [15], who reacted cyclopentadienyl titanium complex $\text{CpTiCl}_2(\text{OEt})$ with HEMA to obtain the Ti-HEMA catalyst. The resulting macromonomer was subsequently copolymerized with MMA by conventional and ATRP radical polymerizations. Among other metal-containing catalysts used in PLA macromonomer synthesis, samarium bromide hexahydrate has to be noted [16].

Another kind of functional polylactide obtained by coordination mechanism was PLA fitted with triple bond. It provided a substrate for “click” reaction, which has recently gained an increasing importance in synthetic polymer chemistry [17]. Such functional polyester was synthesized in the presence of propargyl alcohol as an initiator with tin octoate as a catalyst [18]. Using a diol substituted with propargyl group as an initiator for coordination polymerization (tin octoate as catalyst), Webster obtained a macromonomer containing two PLA chains linked with one triple bond [19].

As it is evident from the presented examples of polylactide macromonomers synthesis, all of them were performed using catalysts based on metal complexes. There are reports on metal-free polymerization of lactide [20–23] but to our knowledge, in the literature there are no examples of cationic polymerization catalyzed by Bronsted acid leading to PLA macromonomers.

In our group, for several years cationic polymerization of oxygen-containing heterocyclic monomers proceeding by Activated Monomer (AM) mechanism has been studied. This method was described in several reviews [24,25]. It suffices to say here that by successive additions of protonated monomer molecules to an HO- group-containing compound acting as an initiator, functional groups present in the initiator molecule are preserved in the growing macromolecule. For several systems it has been shown that $\text{DP}_n = [\text{M}]_0/[\text{I}]_0$ and the dispersity is rather narrow which confirms that the initiation is fast and quantitative. The basic scheme of cationic AM polymerization of oxygen-containing heterocyclic monomers is shown in Scheme 1.

It has been shown that cationic AM polymerization of cyclic ethers is a convenient method of synthesis of reactive polymers (macromonomers, oligodiols) [26–28].

Although there are a few papers describing cationic AM polymerization and copolymerization of lactide, only low molecular weight diols or simple alcohols were used as initiators [8,9,29–32]. Surprisingly, no attempt has been made to employ this simple and experimentally convenient method for the synthesis of reactive lactide polymers other than oligodiols. This approach offers several advantages, as cationic AM polymerization does not require a metal-based catalyst, and trifluoromethanesulfonic acid typically used as a catalyst is easily available and may be easily removed after polymerization by neutralization or washing with water. Moreover, extension of known methods based principally on coordination polymerization to cationic polymerization may allow the synthesis of functional polymers containing reactive end groups that are not stable at the conditions of coordination polymerization but are fully preserved at the conditions of cationic polymerization. This prompted us to look into the possibility of applying cationic AM polymerization of lactide for the synthesis of reactive lactide polymers. Reactive polymers containing double or triple bonds at

the chain end were selected as examples, although in principle this approach may be applied for the synthesis of polymers containing other functional groups, providing that they are stable under acidic conditions.

Thus, in this paper we describe the synthesis of polylactide macromonomers carrying unsaturated (meth)acrylate and propargyl groups at one chain end by cationic polymerization. The reactivity of functional groups was confirmed by radical (co)polymerization of macromonomers or by performing azide-alkyne “click” reaction with a model azide.

2. Experimental

2.1. Materials

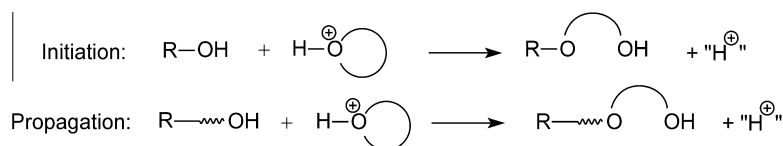
L,L-lactide (LA, Boehringer Ingelheim, Germany) was crystallized from dry 2-propanol and then purified by sublimation in vacuum (10^{-3} mbar, 85 °C). 2-Hydroxyethyl methacrylate (HEMA) (97%, Acros Organics) and 2-hydroxyethyl acrylate (HEA) (96%, Aldrich) were passed through a column filled with Al_2O_3 and distilled after drying over molecular sieves. Methyl methacrylate (MMA) (99%, Aldrich) and *n*-Butyl Acrylate (BuAc) (99%, Aldrich) were distilled under reduced pressure shortly before use. Propargyl alcohol (99%, Aldrich) was stored over molecular sieves and distilled in vacuum before use. Benzyl azide (94%, Alfa Aesar), copper (I) bromide (98%, Aldrich), *N,N,N',N',N''*-pentamethyldiethylene-triamine (PMDTA) (99% Aldrich), trifluoromethanesulfonic acid (triflic acid) (98%, Aldrich), calcium oxide (CaO) (POCH p.a.) and AIBN (98%, Aldrich) were used as received. Dichloromethane (CH_2Cl_2) (POCH, p.a.) and 1,4-dioxane (POCH, p.a.) were dried over CaH_2 and distilled. Toluene (99%, Aldrich) was distilled.

2.2. Synthesis of PLA with HEMA end group (HEMA-PLA)

A general procedure of preparation of functionalized PLA is described using the example given below (No. 1 in Table 1). Freshly purified LA (1.0 g, 6.9 mmol) and CH_2Cl_2 (3.9 mL) were placed in a round-bottom flask. The mixture was degassed by bubbling nitrogen and 100 μL (0.77 mmol) of HEMA was introduced by syringe. During stirring 42 μL (0.47 mmol) of triflic acid was added. The reaction was carried out for 3 h at room temperature and then the acid catalyst was neutralized with CaO. After filtration the solvent was removed and the product was dried under vacuum and characterized by GPC, ^1H NMR and MALDI TOF.

2.3. Synthesis of PLA with propargyl end group (Propargyl-PLA)

As an example the description of PLA No. 7 in Table 1 is given. L,L-lactide 0.9 g (6.24 mmol) was dissolved in 1.5 mL of CH_2Cl_2 in a round-bottom flask. The flask was purged with argon and closed with rubber septum. Then 17 μL (16.5 mg, 0.29 mmol) of propargyl alcohol and next 10 μL (17 mg, 0.11 mmol) of triflic acid were added with a syringe. After 5 h of stirring the polymerization was stopped by neutralization of reaction mixture with about 0.1 g of CaO. The solution was filtered from CaO and the solvent was evaporated. The product was dried on vacuum line.



Scheme 1. Cationic polymerization of oxygen containing cyclic compounds proceeding by activated monomer mechanism.

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