European Polymer Journal 49 (2013) 843–852

Contents lists available at SciVerse ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Grafting onto a renewable unsaturated polyester *via* thiol–ene chemistry and cross-metathesis

Nicolai Kolb, Michael A.R. Meier*

Karlsruhe Institute of Technology, Institute of Organic Chemistry, Fritz-Haber-Weg-6, Building 30.42, 76131 Karlsruhe, Germany

ARTICLE INFO

Article history:
Received 25 August 2012
Received in revised form 22 September 2012
Accepted 27 September 2012
Available online 12 October 2012

Keywords:
Olefin cross-metathesis
thiol–ene
Renewable polyester
Methyl 10-undecenoate
Malonate
Passerini

ABSTRACT

Methyl 10-undecenoate was modified to its corresponding malonate derivative by the reaction with sodium hydride in dimethyl carbonate. This malonate was then polymerized with 1,6-hexanediol, catalyzed by 1.0 mol% titanium (IV) isopropoxide, to a poly(malonate) bearing C_9 aliphatic side-chains with terminal double bonds. The double bonds of this poly(malonate) were used for grafting onto reactions by either ruthenium-catalyzed cross-metathesis reactions with acrylates or thiol–ene addition reactions. Several examples are shown for both methods. For the cross-metathesis reactions, 1.0 mol% Hoveyda–Grubbs 2nd generation (**HG II**) catalyst was used with 10.0 equivalents of the respective acrylate under bulk conditions at 40 °C. The thiol–ene additions were carried out with 1.0 equivalents of the respective thiol in THF with 5.0 mol% 2,2-Dimethoxy-2-phenylacetophenone (DMPA) under UV (365 nm) irradiation. Moreover, we have shown that a carboxylic acid group can be easily installed *via* thiol–ene addition and that the resulting polymer can be further modified by the Passerini three-component reaction with quantitative conversion.

1. Introduction

Considering the decrease of fossil resources, it is one of today's major challenges of chemistry to develop sustainable alternatives for commodity chemicals. In this context, fatty acids have been proven to be a promising resource for polymer chemistry [1,2]. We have recently presented a method for the selective modification of saturated fatty acid methyl esters (FAMEs) towards malonate derivatives by deprotonation of the FAME in α-position with sodium hydride (NaH) in dimethyl carbonate (DMC) as reactive solvent [3]. Most of the other conversions of fatty acids towards renewable polymers have been reported for unsaturated fatty acids. Thus, the double bond within the aliphatic chain is used for diverse chemical modifications, for example, *via* thiol–ene addition reactions [4–10], ruthenium-catalyzed olefin-metathesis [11–17] or isomerization reactions with subsequent modifications [18,19], to only mention some of the more recent examples.

The aim of this project is to expand the scope of the fatty-acid derived malonate polymer synthesis to an unsaturated FAME, namely methyl 10-undecenoate, which bears a C_{11} aliphatic chain with a terminal double bond. The precursor, 10-undecenoic acid, can be synthesized by the pyrolysis of ricinoleic acid, which is the major fatty acid of castor oil [20]. The malonate derivative of this ester and its polyester would still contain a terminal double bond on each side-chain, which allows grafting onto reactions *via* both the ruthenium-catalyzed cross-metathesis and thiol–ene addition reactions to introduce various functional groups in an efficient manner under mild conditions. Similar modifications have been carried out on different polymers *via* thiol–ene addition reactions yielding selectively functionalized polymers. For example, it has been shown that polybutadienes [21,22], polystyrenes or polyesters [23] and polyoxazolines [24,25] bearing short aliphatic chains with terminal double bonds can be used for the modification with different thiols. Thereby, various functional groups (e.g. hydroxyl groups, esters, or carboxylic acids) can be

---

* Corresponding author. Tel.: +49 (0)721 608 48326.
E-mail address: m.a.r.meier@kit.edu (M.A.R. Meier).
URL: http://www.meier-michael.com. (M.A.R. Meier).

0014-3057/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.eurpolymj.2012.09.017

introduced. So far, the described examples almost exclusively covered non-renewable polymers. On the other hand, we recently introduced a new methodology for a versatile grafting onto unsaturated polymers *via* olefin-metathesis with acrylates [26].

Here, we would like to demonstrate the great potential of unsaturated fatty-acid derived poly(malonates) as renewable polymers. Since the double bond within the aliphatic side-chain is still available for modifications, it is possible to selectively introduce functional groups and therefore change the thermal and/or physical properties of this renewable polymer. Furthermore, it is of importance that, by the selective introduction of functional groups, well-defined polymeric structures can be easily prepared, which otherwise might be challenging. Thus, these methods allow a straightforward tuning of polymer structure and therefore also polymer properties.

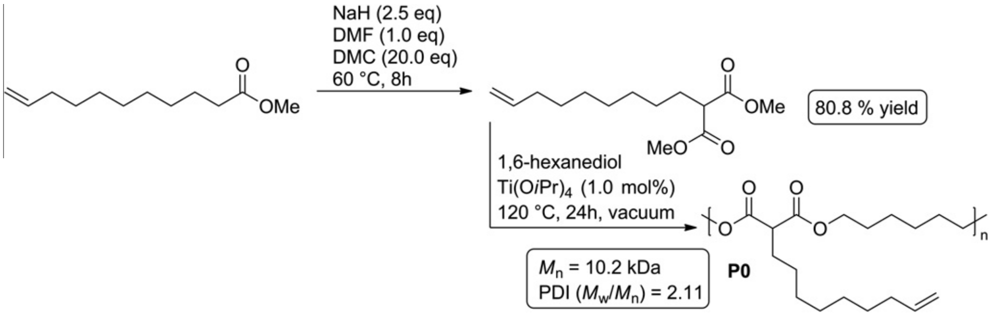
2. Results and discussion

2.1. Preparation of starting polyester (***P0***)

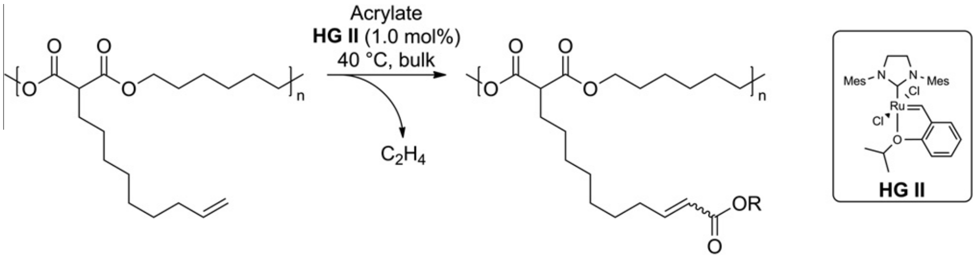
The first step of our investigations was the synthesis of a malonate derivative from unsaturated fatty acids and its polymerization (Scheme 1). We chose the castor oil derived 10-undecenoic acid as the substrate, since it features a terminal double bond, thus offering manifold opportunities for subsequent grafting onto chemistry. For the malonate synthesis we used our recently described procedure [3] with 2.5 equivalents of sodium hydride and 1.0 equivalent DMF in 20.0 equivalents of dimethyl carbonate as reactive solvent. This reaction yields the unsaturated malonate derivative in 80.8% yield on a multiple gram scale. The polymerization of the resulting malonate monomer was then carried out with 1,6-hexanediol and 1.0 mol% titanium isopropoxide under bulk conditions under high vacuum at 120 °C. The obtained polymer was precipitated in ice-cold methanol. The resulting poly(malonate) had an average molecular weight of 10.2 kDa and was obtained as a yellow, highly viscous oil. Differential scanning calorimetry showed a glass-transition of this polymer at −74.1 °C, which corresponds with our earlier studies on saturated poly(malonates) [3].

2.2. Cross-metathesis with acrylates

We investigated the modification of **P0** *via* ruthenium-catalyzed cross-metathesis with acrylates (type II olefins), which exhibit excellent cross-metathesis selectivity with terminal olefins (Scheme 2) [27]. We chose the Hoveyda–Grubbs catalyst 2nd generation (**HG II**) catalyst [28], since this catalyst gave best results in our earlier studies on the cross-metathesis of methyl 10-undecenoate with methyl acrylate (**MA**) [11]. The first experiments were carried out on a 0.5 mmol (155 mg) scale in 1 mL of dichloromethane (DCM) with 1 mol% catalyst loading and 5–10 equivalents of **MA**. Although we achieved complete conversion of the terminal double bonds, GPC analysis showed coupling of the polymer *via* self-metathesis (Table 1, entries 1–2). Therefore, we tried to carry out the reaction under bulk conditions with 10 equivalents of **MA** to avoid DCM as solvent and suppress the polymer–polymer coupling side-reaction yielding complete conversion of the terminal double bond without cross-linking (Table 1, entry 3). With 5 equivalents of **MA** under bulk conditions, only 67% conversion was achieved and polymer–polymer coupling took



Scheme 1. Synthesis of malonate derivative and starting polymer **P0**.



Scheme 2. Polymer-functionalization *via* ruthenium-catalyzed olefin-metathesis.