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Synthesis of polyacrylates from limonene by catalytic oxidation and multi-component reaction



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ABSTRACT

A new strategy to obtain polyacrylates from limonene *via* regioselective catalytic acetoxylation, catalytic isomerization and subsequent Passerini three-component reaction (P-3CR) is described. The acetoxyated limonene derivative, selectively functionalized at the exocyclic double bond, was synthesized by a palladium-catalyzed C-H activation process in the presence of *para*-benzoquinone (BQ) as reoxidation agent and acetic acid in dimethyl sulfoxide. The obtained product was further saponified and subsequently isomerized under mild conditions into the corresponding aldehyde using a hydrogen-activated palladium catalyst. The resulting aldehyde, acrylic acid and various isocyanides were then used in the Passerini three-component reaction (P-3CR) in order to obtain several acrylate monomers in a straightforward and atom economic process. In subsequent free radical polymerizations using AIBN as thermal initiator, polyacrylates with molecular weights (M_n) up to 30 kDa were obtained and carefully characterized by SEC, NMR and DSC analysis.

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1. Introduction

The challenge to find sustainable solutions in terms of environmental concerns as well as raw material availability has become a major focus in polymer chemistry in recent years [1]. The tremendous potential of cellulose, lignin, sugars as well as fats and oils in this regard is already demonstrated by the use of more than nine million tons per year of these renewable raw materials by the European industry [2]. Among the available renewable materials, also terpenes constitute a valuable and cheap biomass resource, which can be obtained in large amounts from various essential oils or as by-product from diverse industrial processes [3–5]. Terpenes are also widely synthesized in nature as secondary metabolites by plants, fungi and microorganisms and offer versatile functionalization possibilities, due to their remarkable structural diversity. As a result, terpenes exhibit diverse properties and thus finds manifold applications, e.g. for flavors, fragrances, nutrients, pheromones or as pharmacological substrates in treatments of different diseases [6–8]. Limonene, a naturally occurring dipentene (present as L-(–)-limonene in noble fir or as L-(+)-limonene in the peels of citrus fruits), is one of the many terpenes considered as valuable renewable feedstock [9]. Interestingly, the annual world production of citrus fruits has been estimated to be 88×10^6 tons per year, whereby D-(+)-limonene can be obtained as a waste product in considerable amounts (>90%) from orange peel oil [4]. Chemically of interest, limonene incorporates an exocyclic- and an endocyclic double-bond in its structure. The most straightforward approach to polymerize natural terpenes is their direct cationic polymerization by

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living or conventional mechanism, as it was already investigated by Robert and Day in 1950 [10]. The homo-polymerization of D-(+)-limonene into poly(D-(+)-limonene) was also conducted in 1965 by Marvel and coworkers using a Ziegler-Natta catalyst [11]. However, applying the aforementioned protocols, only low molecular weights of 1200 g mol^{-1} were obtained. The free radical copolymerization of limonene with *N*-vinyl pyrrolidone [12] as well as methyl methacrylate [13] or styrene [14] was reported by Sharma and Srivastava. Moreover, Shiono and coworkers have described a protocol for the copolymerization of limonene with ethylene using a titanium catalyst. However, low molecular weights were achieved if compared to ethylene homopolymerization or copolymerization of ethylene with isobutylene [15]. Nakatani et al. studied a different approach to incorporate limonene. For this purpose, poly(1-butene) was modified *via* a free-radical graft polymerization process in order to introduce functional groups along the polymer backbone [16]. Due to their unsaturated cyclic structures, ring-opening metathesis polymerization (ROMP) constitutes a key polymerization methodology of terpenes. Mathers et al. published a ROMP protocol for the preparation of functional hyperbranched polymers from dicyclopentadiene with limonene as well as limonene oxide using an appropriate Grubb's catalyst [17]. Additionally, in former studies the same group clearly demonstrated that limonene is acting as a green solvent as well as a chain-transfer agent in ROMP. Another very interesting modification of limonene is accomplished by free-radical thiol-ene chemistry [18]. Recently, Meier et al. described the efficient synthesis of limonene-based polyesters, polyamides as well as non-isocyanate polyurethanes (NIPU's) *via* solvent and initiator-free thiol-ene addition [19,20]. Johansson et al. have taken advantage of this concept using limonene in the presence of polythiols to synthesize thermoset coatings under thermal and photoinitiated conditions [21]. Moreover, in order to broaden the use of terpenes, the development of catalytic and selective oxidation processes is of great interest and allows access to potential new precursors for polymer chemistry. Howdle et al. recently reported the synthesis and further radical polymerization of new renewable-based acrylates from monoterpenes. The acrylate monomers were first synthesized *via* a non-sustainable two step procedure, starting with a hydroboration/oxidation or reduction process, by employing (meth)acryloyl chloride afterwards. Further investigations were carried out on a one-pot greener catalytic approach, using a palladium-catalyzed oxidation process to couple β -pinene with methacrylic acid, yielding β -pinene derived methacrylates with up to 82% yield [22]. Inspired by a different catalytic approach, we have started our investigations on the synthesis of polyacrylates using limonene as a renewable raw starting material. For this purpose, we focused on a regioselective catalytic acetoxylation process that allows access to a precursor for the synthesis of an aldehyde derivative, which was then employed in the Passerini three-component reaction. Thus, by simple variation of the isocyanide component in this multi-component reaction, different acrylate monomers were obtained and subsequently studied in a free-radical polymerization process to lead to polymers with different thermal properties.

2. Experimental section

2.1. Materials

Acetic acid (>96%, Roth), 2,2'-azobis(2-methylpropanitrile) (98%, Sigma Aldrich), benzyl isocyanide (98%, Sigma Aldrich), *p*-benzoquinone (>98%, Sigma Aldrich), *tert*-butyl isocyanide (98%, Sigma Aldrich), chloroform-*d* (CDCl_3 , 99.8 atom % D, Armar Chemicals), cyclohexyl isocyanide (98%, Sigma Aldrich), dimethyl sulfoxide (DMSO, >99.5%, Roth), ethyl isocyanacetate (95%, Sigma Aldrich), hydrogen (>99.999, Air Liquid), (*S*)-(–)-limonene (96%, Sigma Aldrich), palladium(II) acetate (98%, Sigma Aldrich), palladium hydroxide on carbon (20 wt.% loading on dry weight, Sigma Aldrich), *n*-pentylisocyanide (97%, Sigma Aldrich), sodium sulfate (>99% anhydrous, Acros Organics), sodium hydrogen carbonate (>95%, Sigma Aldrich), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%, Sigma Aldrich), tetradecane (>99%, Sigma Aldrich), silica gel 60 (0.040–0.063, Sigma Aldrich), TLC silica gel F254 (Merck), potassium permanganate (>99%, Sigma Aldrich), potassium carbonate (99.7%, Sigma Aldrich), sodium hydroxide (98%, Sigma Aldrich), molecular sieve (3 Å, Sigma Aldrich), dichloromethane, ethyl acetate, *n*-hexane, methanol, toluene. All solvents were used without further purification.

2.2. Synthesis of **2** from limonene

The acetoxyated products were prepared according to a procedure described recently [23]. 200 mg (1.47 mmol, 1.00 eq) (*S*)-(–)-limonene **1** were dissolved in 1.5 mL DMSO and 1.5 mL acetic acid. Additionally, 160 mg (1.47 mmol, 1.00 eq) *p*-benzoquinone, 250 mg molecular sieve (3 Å) and 29.0 mg (0.15 mmol, 10.0 mol%) *n*-tetradecane (internal standard) were added and the mixture was stirred for five minutes at 50 °C. Then, 13.2 mg (0.06 mmol, 4.0 mol%) of palladium(II) acetate was added and the mixture was stirred for 24 h at 50 °C. The crude mixture was washed with water, sodium hydrogen carbonate and brine, dried over sodium sulfate and evaporated to dryness. Afterwards, the crude product was purified *via* column chromatography (hexane/ethyl acetate 95:5) to afford an orange-yellow liquid. The obtained product was a mixture of the major product **2**, which was used for further reactions and small amounts of the by-products **3*** and **4***.

2.3. Synthesis of allylic alcohol **5** derived from **2**

0.50 g (2.57 mmol) of **2** and 18.0 mg (0.13 mmol, 0.05 eq) of TBD were dissolved in 20.0 mL of methanol and stirred under reflux for six hours at 90 °C. After cooling to room temperature, the reaction mixture was washed with water, sodium

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