Macromolecules
ARTICLE
pubs.acs.org/Macromolecules

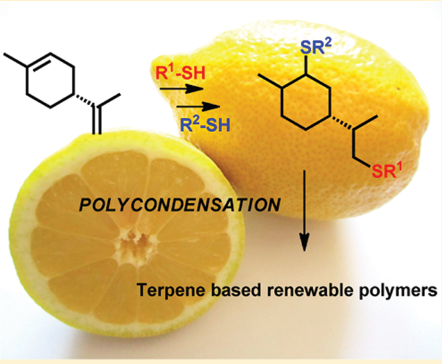
Terpene-Based Renewable Monomers and Polymers via Thiol−Ene Additions

Maulidan Firdaus, Lucas Montero de Espinosa, and Michael A. R. Meier*

Institute of Organic Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 6, 76131 Karlsruhe, Germany

S *Supporting Information*

ABSTRACT: Solvent and radical initiator-free addition of thiols to terpenes ((*R*)-(+)- and (*S*)-(−)-limonene and (−)-*β*-pinene) are described as a simple approach to obtain a wide range of alcohol and/or ester functionalized renewable monomers. (*R*)-(+)-Limonene (**1**) and (*S*)-(−)-limonene (**2**), presenting different reactivity at the endocyclic and exocyclic double bonds, have yielded the mono-addition or diaddition product by simple variation of the thiol feed ratio. In the same manner, (−)-*β*-pinene (**3**) derived alcohol and ester monomers have been prepared. The monomers thus obtained have been characterized, and their behavior in polycondensation has been studied. It has been found that long chain diesters or diols, which were synthesized from a castor oil derived platform chemical, are suitable comonomers and result in polycondensates with number-average molecular weights of up to 25 kDa. Thus, terpene/fatty acid-based polyesters were prepared, and their structure−thermal property relationships were studied.

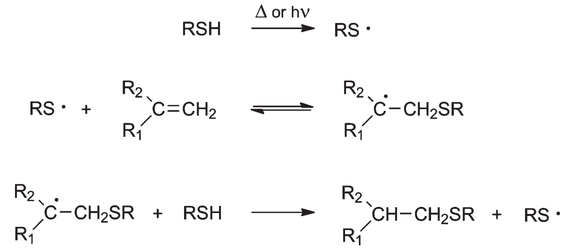


INTRODUCTION

The utilization of renewable resources for the synthesis of new platform chemicals has been accepted as a great challenge in order to contribute to a sustainable development.[1,2] Among the wide variety of available renewable resources, terpenes are found in many essential oils and represent a versatile chemical feedstock.[3] α-Pinene and *β*-pinene are the major components of wood turpentine, which can be obtained from the resinous sap of pine trees by steam distillation. It is also one of the main byproducts of the Kraft process, which is used in the paper industry to extract lignin from wood in the production of pulp.[4] Limonene can be obtained as a byproduct of the citrus industry and is a very common terpene, being produced by more than 300 plants.[5] The (*R*)-enantiomer represents 90−96% of citrus peel oil,[6] and its world production is over 70 000 tons per year.[7] In contrast to many other terpenes, pinenes and limonenes are abundant and inexpensive natural compounds that are real building blocks for the synthesis of new important chemicals for use as fragrances, flavors, pharmaceuticals, solvents, and chiral intermediates.[3,8]

Known chemical transformations of these renewables were extensively reviewed by Corma et al.,[3] including isomerization, epoxidation, hydration, or dehydrogenation reactions among others. The isomerization of terpenes provides a wide range of products such as camphene, which is produced industrially by isomerization of α-pinene and is used as an intermediate in the chemical industry for production of fragrance compounds, terpene−phenol resins, and other derivatives. The hydration of α-pinene or turpentine oil with aqueous mineral acids yields *cis*-terpin hydrate, which can be partially dehydrated into α-terpineol, the most important monocyclic monoterpenic alcohol and the one most used as a fragrance in soaps and cosmetics due to its typical lilac odor. The selective epoxidation of limonene leads to limonene oxide, which is found in natural sources and used in fragrances. It is also an active cycloaliphatic epoxide with low viscosity that can be used with other epoxides in applications including metal coatings, varnishes, and printing inks.

Scheme 1. Mechanism of Radical Thiol−Ene Additions



Thiol−ene chemistry, although already known for more than 100 years,[9] has not been studied in detail using terpenes as olefinic substrates. It proceeds via a free radical chain mechanism and mainly yields the anti-Markovnikov products.[10] First, the initially formed thiyl radical attacks the unsaturated substrate forming a carbon radical. The carbon radical then reacts with a thiol molecule to give the final product and a new thiyl radical, thus propagating the radical chain (Scheme 1). Since this

Received: July 19, 2011
Revised: August 3, 2011
Published: August 18, 2011

dx.doi.org/10.1021/ma201544e | *Macromolecules* 2011, 44, 7253–7262

involves the cleavage of a S—H bond, the overall reaction rate will be strongly influenced by the structure of the thiol and the lifetime of the intermediate carbon radical. Moreover, the C—S bond formation is a reversible process which also depends on the structure of the olefin. Thus, the addition of thiols to terminal olefins, monosubstituted alkynes, and olefins leading to resonance stabilized radical intermediates is less reversible than the addition to internal olefins.[10] Therefore, terminal double bonds are generally more reactive than internal ones.[11]

Nowadays, thiol—ene additions are widely used as very efficient transformations since in many cases they display click reaction features[12] and are thus versatile tools for the preparation of value-added chemical intermediates.[13,14] Thiol—ene additions can be performed under mild reaction conditions by simply mixing thiols and olefinic substrates if terminal olefins are used. Moreover, the products are generally obtained in high yields with low byproduct formation. The addition of thiols to less reactive olefins can be initiated thermally with radical initiators or with radical photoinitiators in presence of UV irradiation.

Even though thiol—ene reactions have been studied for a long time, covering different scientific fields from biochemistry to polymer science, only very few examples have been reported on thiol—ene additions with terpenes as olefinic substrates. In 1957, Marvel and Olson described the synthesis of a terpene-based dithiol by addition of thioacetic acid to (*R*)-limonene.[15] They subsequently used this dithiol in the synthesis of polyalkylene sulfides via thiol—ene polymerization with the original (*R*)-limonene. The obtained poly(alkylene sulfide)s were soft and sticky with inherent viscosities in the 0.12—0.36 range. Later on, the addition of hydrogen sulfide to limonene was shown by Tolstikov et al. to give menth-1-ene-8-thiol, characteristic of the grapefruit flavor.[16] The same researchers reported that this compound is also obtained by the Lewis acid catalyzed addition of hydrogen sulfide to pinenes.[17] More recently, Janes et al. reported the synthesis of several terpene-based thiols by reaction of hydrogen sulfide with different monoterpenoids, observing in some cases the formation of bridged *epi*-sulfides as minor products.[18] Overall, the knowledge about the reactivity of terpenes toward thiol additions is thus limited. However, the high efficiency of thiol—ene additions, which permits the introduction of different functionalities to olefinic structures, makes it a suitable way to obtain terpene-based monomers for the synthesis of renewable polymers.

In this aspect, terpenes have been used since long as renewable monomers and precursors of monomers in polymer synthesis through many different approaches.[19] Moreover, since terpenes can be obtained from nature as pure enantiomers, the chiral polymers derived from them have potential applications in chiral purification,[20] in asymmetric catalysis,[21] in nonlinear optics,[22] or as conducting materials.[23] The cationic polymerization of β-pinene has been intensively studied in presence of several Lewis acids at temperatures between −80 and 0 °C in order to avoid chain transfer.[24] Among them, $EtAlCl_2$ was shown to be the most efficient one producing polymers with molecular weights up to 40 kDa.[25] The cationic polymerization of β-pinene has also been achieved in a living manner by Lu et al., who prepared block copolymers of β-pinene with styrene or *p*-methylstyrene (PDI as low as 1.2) using isopropoxytitanium trichloride and tetra-*n*-butylammonium chloride at −40 °C.[26] The radical homopolymerization of monoterpenes is an inefficient process that leads to oligomers with molecular weights below 1000 Da;[27] however, when they are used as comonomers in free radical polymerizations, high molecular weight polymers can be obtained. Thus, β-pinene has been successfully copolymerized with styrene,[24b] methyl methacrylate,[27] acrylonitrile,[28] maleimide,[29] or a sucrose-based monomer[30] to name a few examples. Likewise, limonene has been radically copolymerized by Sharma and Srivastava with styrene,[31] methyl methacrylate,[32] acrylonitrile,[33] *N*-vinylpyrrolidone,[34] and other comonomers.[19] Regarding the polymerization of terpene derivatives, Aikins and Williams reported the radiation-induced cationic polymerization of limonene oxide, α-pinene oxide, and β-pinene oxide, which led to low molecular weight polyethers with high monomer conversions.[35] More recently, Coates and co-workers reported the syntheses of alternating polycarbonate copolymers of (*R*)-limonene oxide and carbon dioxide using β-diiminate zinc complexes.[36] This work was the first example of a non-petroleum route to carbon dioxide copolymers.

Within this work, we aim to extend the current knowledge on the reactivity of naturally occurring terpenes toward thiol additions and to establish the reaction conditions that maximize their efficiency. Furthermore, we present thiol—ene terpene modification as a suitable tool to obtain renewable monomers for the synthesis of polyesters.

■ RESULTS AND DISCUSSION

Syntheses of Monomers. As discussed in the Introduction, despite the large amount of work that has been done on the chemical transformation of terpenes for the synthesis of industrially valuable chemicals, building blocks, or monomers for polymer synthesis, the thiol—ene reaction using limonene and pinene as olefinic substrates has not been fully explored yet, and only a few studies have been reported. The reaction of these abundantly available terpenes with functional thiols is attractive since it can provide chiral monomers in a one-step procedure directly from a renewable feedstock. More specifically, the extensive reaction of both double bonds of limonene with hydroxyl or methyl ester functionalized thiols would lead to suitable monomers for polycondensation. On the other hand, the reaction of pinene with these functional thiols would lead to terpene-based building blocks that could be used for the synthesis of grafted polymers following a grafting-onto approach or for the synthesis of monomers of higher complexity. Furthermore, the different reactivity of the double bonds of limonene toward thiol additions can be exploited to selectively functionalize the more reactive exocyclic (terminal) double bond, leaving the endocyclic (internal) one unreacted for further transformations. It is worth to highlight the simplicity of these reactions, which can usually be performed by simply mixing thiol and olefin in the absence of solvent and radical initiator and at temperatures close to room temperature.[37]

Taking this information, we started by studying the solvent-free, radical initiator-free thiol—ene addition of 2-mercaptoethanol (**4**), methyl thioglycolate (**5**), and thioglycerol (**6**) to (*R*)-(+)-limonene (**1**), (*S*)-(−)-limonene (**2**), and (−)-β-pinene (**3**) at room temperature (Scheme 2). During the course of our investigations, we found that **5** shows a higher reactivity than **4** and **6**. For this reason, in the following discussion, the results of the thiol—ene additions using **5** will be addressed separately since a more thorough optimization of the reaction conditions was needed. The high reactivity of thiols based on glycolate esters has been observed before and was ascribed to a weakening of the thiol bond by formation of a hydrogen bond with the carbonyl

Scheme 2. Mono- and Diadditions of Thiols 4−6 to Terpenes 1−3

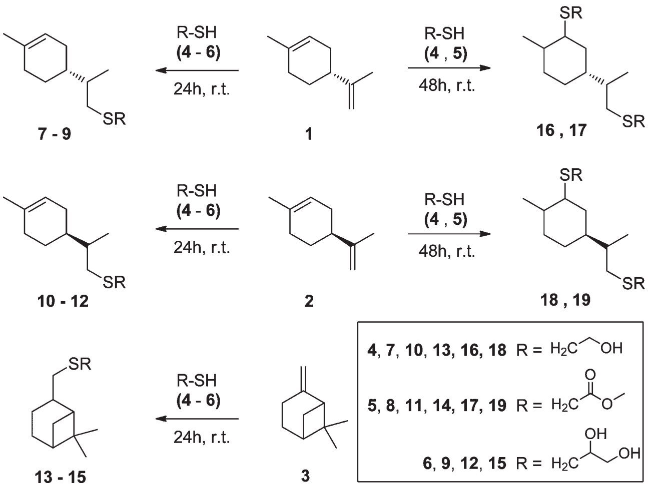


Table 1. Results of Monoaddition of Thiols 4−6 to Terpenes 1−3[a]

terpene	thiol	product	yield (%)[b]
1	**4**	**7**	85
1	**5**	**8**	55
1	**6**	**9**	80
2	**4**	**10**	82
2	**5**	**11**	52
2	**6**	**12**	61
3	**4**	**13**	81
3	**5**	**14**	60
3	**6**	**15**	76

[a] Reaction conditions: terpene:thiol ratio 1:1.2, rt for 24 h. [b] After column chromatography.

Table 2. Results of Diadditions of Thiols 4−6 to Terpenes 1 and 2 and Additions of 4 and 5 to Monoaddition Products

terpene	thiol (equiv)	product	yield (%)[d]
1	**4** (2.5)[a]	**7** + **16**	36 (**7**); 62 (**16**)
1	**5** (2.5)[a]	**8** + **17**	5 (**8**); 93 (**17**)
1	**6** (2.5)[a]	*e*	
2	**4** (2.5)[a]	**10** + **18**	11 (**10**); 82 (**18**)
2	**5** (2.5)[a]	**11** + **19**	4 (**11**); 93 (**19**)
2	**6** (2.5)[a]	*e*	
7	**5** (2.0)[b]	**20**	83
8	**4** (1.2)[c]	**21**	92
10	**5** (2.0)[b]	**22**	81
11	**4** (1.2)[c]	**23**	90

[a] At rt for 48 h. [b] At rt for 72 h. [c] At rt for 24 h. [d] After column chromatography. [e] Only the monoaddition product was obtained.

group.[13] With the exception of additions of **5**, the rest of the reactions were performed under vacuum (200 mbar) in order to remove oxygen,[37] which is an efficient radical scavenger in these reactions. First, the thiol−terpene ratio was optimized to maximize the efficiency of the monoaddition reactions. Initially, a 1:1 ratio was used for the addition of **4** and **6** to **1**, **2**, and **3**. However, the conversion of the double bonds was rather low (below 50%), even after 48 h. When the amount of thiol was increased to 1.2 equiv, the double bond conversions also increased, and 60−80% isolated yields of monoaddition products were obtained after column chromatography (see Table 1). Interestingly, the addition of **4** and **6** to **1** and **2** took place exclusively at the exocyclic double bond, and no diaddition products were observed. On the other hand, the addition of **5** to **1** and **2** showed a lower selectivity, giving additions both to the exocyclic and endocyclic double bonds when working in a 1:1 ratio. Moreover, low double bond conversions were obtained even after 24 h (below 75%). Also for the addition of **5**, the use of a thiol excess (1.2 mol equiv) provided better results, leading to yields ranging from 52 to 85% after column chromatography (Table 1), but also to a decrease in the regioselectivity (from 74 to 55%). A thiol−terpene ratio of 0.9:1 was then tried in order to favor monoaddition; although it gave a slight increase of regioselectivity (77%), the isolated yield dropped ∼10%. An increase of the temperature to 35 °C gave only a very slight increase in conversions (below 5% increase) and at the same time generally led to a drop of regioselectivity. All thiol−ene additions were also performed in the presence of AIBN at 70 °C. Adding a radical initiator resulted in faster conversion of the terpenes; however, it also resulted in lower regioselectivities, and the conversion rates decreased at reaction times above 5 h, which is about the half-life time of AIBN. As a summary, Table 1 shows the results obtained after optimization of the reaction conditions for the thiol−ene monoadditions and clearly reveals that the exocyclic double bond of limonene can be addressed regioselectively in these radical additions.

Once the thiol−terpene monoadditions were optimized, we focused on the synthesis of the diaddition products of thiols **4**, **5**, and **6** to terpenes **1** and **2** (Scheme 2), for which a thiol−terpene ratio of 2.5:1 was used. The addition of **6** to both **1** and **2** did not give the diaddition products, and only the monoadditions to the exocyclic double bonds were observed, probably due to steric hindrance around the endocyclic double bonds. The additions of **4** and **5** led to a mixture of mono- and diaddition products with conversions over 97% (Table 2). As already mentioned, the monoaddition products from (*R*)-(+)- and (*S*)-(−)-limonene can undergo a second thiol addition with a different thiol to obtain heterodifunctional monomers. Thus, the alcohol functionalized products **7** and **10** were reacted with methyl thioglycolate, and the ester functionalized products **8** and **11** were reacted with 2-mercaptoethanol (Scheme 3). The reactions were conducted at room temperature, in the absence of solvent and radical initiator, and using 2-fold and 1.2-fold excesses of methyl thioglycolate and 2-mercaptoethanol, respectively. In this way, difunctional monomers containing both ester and alcohol groups (**20**−**23**, Table 2) were obtained.

Characterization of Monomers. The terpenes used in this study are pure enantiomers. The addition of one molecule of thiol to the exocyclic double bond of **1** or **2** or to the double bond of **3** generates a new stereogenic center and, thus, two different diastereomers of each product. The addition of a second thiol molecule to the endocyclic double bond of **1** or **2** generates two additional stereogenic centers, increasing the number of possible diastereomer to eight. However, the cyclic and bicyclic structures of these terpenes, together with the fact that they are pure enantiomers, favor the formation of certain diastereomers over others as a result of preferential sides for the thiol approach during the hydrogen abstraction process. Nevertheless, complex

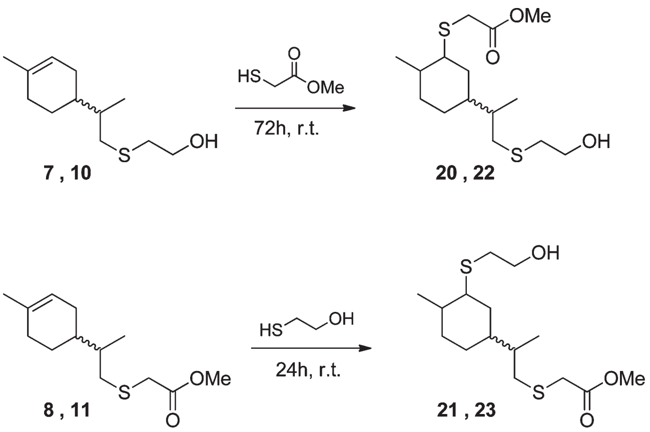
NMR spectra were obtained for all addition products and conventional two-dimensional NMR experiments (COSY, HSQC, and HMBC) were necessary for full assignment.

The presence of diastereomers, which could not be isolated by column chromatography, was also observed in the GC-MS chromatograms of the purified monoaddition products to **1**, **2**, and **3**, where (although not always) two peaks can be observed. For instance, the chromatogram of **14** shows two peaks with different intensities (see Supporting Information), indicating that after the initial thiol addition the approach of a second thiol to the carbon-centered radical, and thus the hydrogen abstraction, takes place preferably from one side. The GC chromatograms of the purified diaddition products to **1** and **2** present several peaks of different intensities as a result of the partial diastereoselectivity in the hydrogen abstraction (see Supporting Information for chromatograms of **17** and **19**).

The analysis of the NMR spectra of these products further confirmed the presence of diastereomers. Moreover, in some cases, the integration of the ^{1}H NMR signals allowed calculating the ratio of the diastereomers. For instance, Figure 1a shows the ^{1}H NMR spectrum of **7** (addition of 2-mercaptoethanol to *R*-(+)-limonene), in which the region of methyl groups bonded to the new stereogenic center is highlighted (for full assignment see experimental part). The methyl groups of both diastereomers appear as doublets of equal intensity, which merge in a false triplet, indicating a 1:1 ratio between both diastereomers. A different case can be observed in Figure 1b, which shows the ^{1}H NMR spectrum of **13** (addition of mercaptoethanol to (−)-*β*-pinene). As can be seen, the signals of the methyl groups attached to the bicyclic backbone present different chemical displacements in both diastereomers. The integration of these signals reveals a ratio of 5:1 between the diastereomers, which confirms that the hydrogen abstraction is stereoselective. In order to determine which one of the two possible diastereomers is the major, we performed a NOE experiment (see Supporting Information), which showed correlation between the protons H^e and H^d of the major diastereomer. This confirms that the approach of the second thiol, and thus the hydrogen abstraction, preferentially takes place from the opposite face to the methyl groups due to steric hindrance.

The ^{1}H NMR spectrum of **17** (diaddition of methyl thioglycolate to *R*-(+)-limonene) shows a higher complexity due to the higher number of possible diastereomers (Figure 2a). In this case, the analysis of the ^{13}C NMR is more helpful in order to determine the number of diastereomers present in the diaddition product and to estimate their ratio. Figure 2b shows the region from 53 to 51 ppm, in which four different signals are observed

Scheme 3. Addition of Thiols 4 or 5 to Monoaddition Products



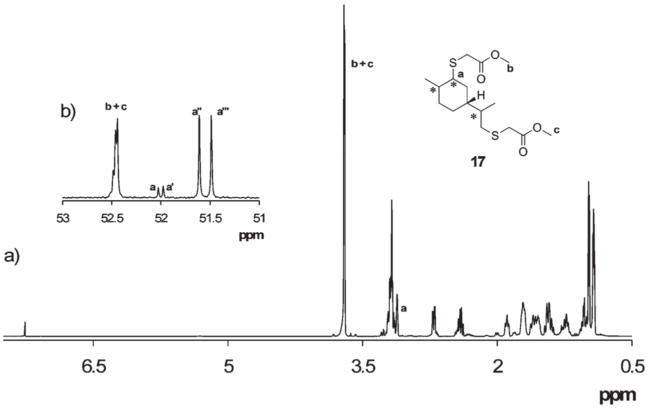


Figure 2. (a) ^{1}H NMR and (b) ^{13}C NMR (region 53−51 ppm) of **17**.

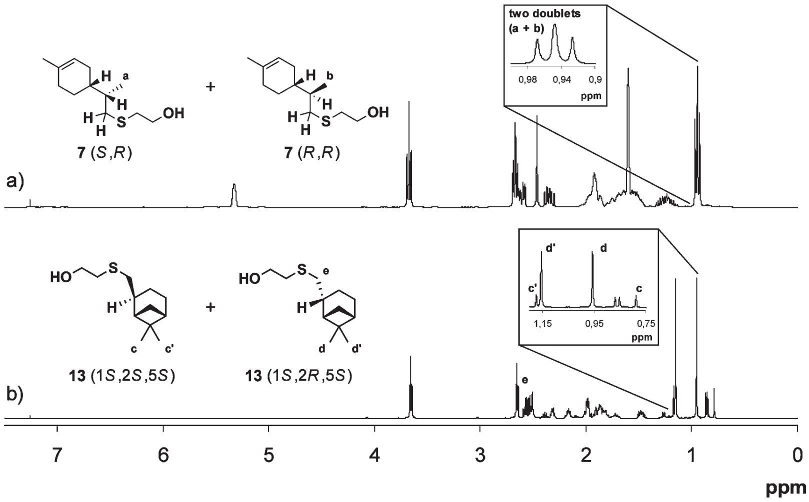
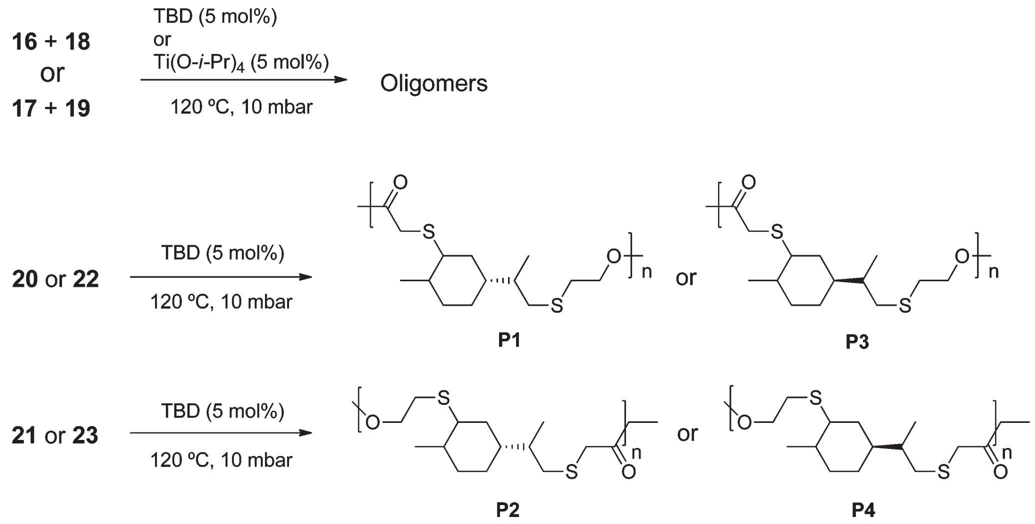


Figure 1. ^{1}H NMR spectra of (a) **7** and (b) **13**.

Scheme 4. Polymerization of Difunctional Monomers and Homopolymerization of Heterodifunctional Monomers



for C_a, indicating that the product mainly consists of a mixture of four diastereomers.

Polymerization Studies. The difunctional monomers obtained by diaddition of 2-mercaptoethanol or methyl thioglycolate to (*R*)-(+)-limonene or (*S*)-(−)-limonene were subsequently used for polyester synthesis. The purity of these monomers was >99% by GC analysis; no monofunctional byproduct were detected that could act as chain-stoppers. 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) was chosen as polycondensation catalyst based on our own experience and on previous reports on its high tranesterification activity.[38] The removal of methanol strongly determines the efficiency of TBD-catalyzed transesterification and can be carried out applying a continuous stream of an inert gas such as nitrogen or constant vacuum in the case of polymerizations. Thus, we performed the polymerizations in presence of 5 mol % (related to ester groups) TBD at 100 and 120 °C under continuous vacuum for 7 h. Initially, diesters **17** and **19** were polymerized with diols **16** or **18** at 200 mbar for 7 h; however, oligomers of 3 kDa were obtained (Scheme 4), probably due to the bulky cyclic structures of both monomers, which could hinder the catalysts' approach and thus decreasing the polymerization efficiency. Moreover, longer reaction times did not lead to an increase of the molecular weight. Titanium isopropoxide was also tried in an attempt to reach higher molecular weights. Titanium alkoxides are known to act as efficient transesterification catalysts and have been successfully used for polyester synthesis[39] being compatible with a variety of functional groups.[40] Moreover, titanates are recognized as extremely powerful for ester-exchange reactions.[41] However, using 5 mol % of titanium isopropoxide under continuous vacuum and 100 or 120 °C provided only slightly higher molecular weights (up to 4 kDa) after 7 h (longer reaction times did not lead to higher molecular weights). The polymerization of heterodifunctional monomers **20**−**23** was then attempted in presence of TBD (Scheme 4). Interestingly, despite having very similar structures to the above-mentioned diesters and diols, the polycondensation of these monomers at 120 °C under continuous vacuum for 7 h led to homopolymers with higher molecular weights (M_n) between 8 and 10 kDa (see Table 3 for data of precipitated polymers). During polycondensations, little deviations from an ideal 1:1 ratio between monomers can substantially decrease molecular weights through a chain-stopper effect. Monomers **20**−**23**, which do not need comonomers, are thus more likely to reach high molecular weights. However, also here, the sterical hindrance caused by the terpene core might reduce the activity of the catalyst.

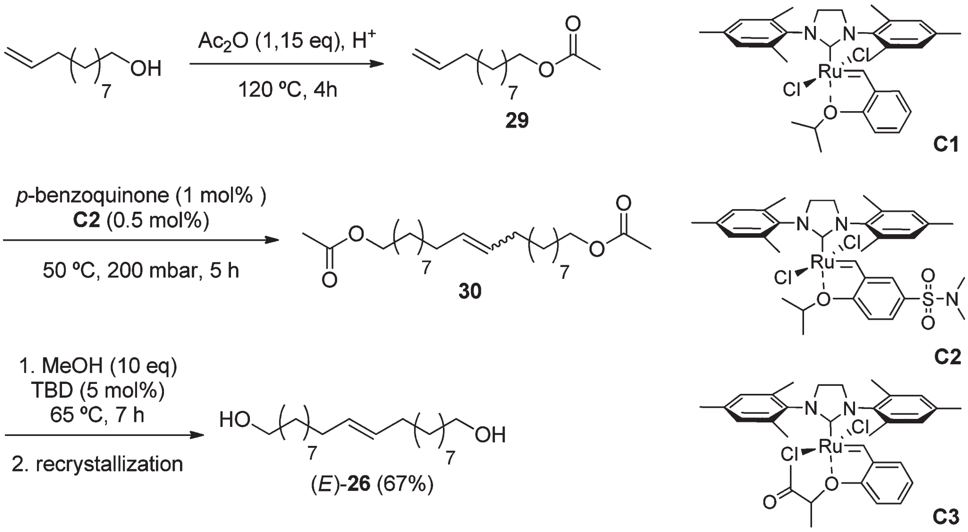
Table 3. Analytical Data of Synthesized Limonene-Based Polyesters[a]

polymer (monomer)	M_n (kDa)	PDI	T_g (°C)[b]
P1 (**20**)	9.3	1.79	−9.7
P2 (**21**)	7.7	1.66	−9.2
P3 (**22**)	10.5	1.89	−10.4
P4 (**23**)	8.2	1.65	−9.9

[a] GPC and DSC data of precipitated polymers. [b] DSC data recorded at 10 °C/min; results from the second heating scan.

From these results, it can be concluded that in order to obtain high molecular weight polyesters from limonene-based diesters and diols, comonomers providing spacing between terpene units might be needed. First, diesters **17** and **19** were polymerized with 1,3-propanediol and 1,6-hexanediol in the presence of 5 mol % of TBD. The polymerizations, which were also performed at 100 and 120 °C and 200 mbar vacuum, only yielded oligomers below 5 kDa. Moreover, substituting TBD by titanium isopropoxide (5 mol %) in the same reaction conditions provided only slightly higher molecular weights (up to 7 kDa) and broad polydispersities. All polymerizations were performed for 7 h, since longer reaction times did not further increase the molecular weights. These results suggested that comonomers with longer alkyl chains between the reactive groups might be needed due to steric reasons. To prove this, suitable diester (**24** and **25**, Scheme 6) and diol (**26** and **27**, Scheme 6) monomers were prepared via self-metathesis or thiol−ene homocoupling of methyl-10-undecenoate and 10-undecen-1-ol. It is worth to mention that both platform chemicals are castor oil derived, and thus, the monomers obtained thereof are also renewable. The presence of double bonds affects both crystallinity and thermal stability of polymers, and for this reason, unsaturated

Scheme 5. Synthesis of Fatty Acid Derived 1,20-Diol 26 and Metathesis Catalysts Studied



diester **24** was reduced to its saturated counterpart (**28**, Scheme 6) in order to compare the thermal properties of the polyesters derived from them. Diesters **24**[42] and **25**[37] and diol **27**[37] were prepared as previously reported. The synthesis of diol **26** was carried out via self-metathesis of 10-undecen-1-ol (Scheme 5). Olefins containing alcohol groups, such as 9-decen-1-ol,[43] have been reported to give moderate yields during metathesis reactions due to formation of side products and/or degradation of the catalyst.[44−46] In this regard, alcohol protection was shown to be helpful in overcoming this drawback.[47] Moreover, we have already shown that acetylation of oleyl alcohol and subsequent cross-metathesis reactions were more efficient, in terms of both catalyst load and produced waste, than using oleyl alcohol directly.[48] Therefore, we followed the same strategy and protected 10-undecen-1-ol by reaction with acetic anhydride to obtain 10-undecenyl acetate (**29**, Scheme 5). After purification by simple filtration through silica gel, the behavior of **29** in self-metathesis was studied. Three different metathesis catalysts were tested (Scheme 5), namely Hoveyda−Grubbs second generation (**C1**), Zhan (**C2**), and Umicore 5_1 (**C3**), to obtain the desired self-metathesis product **30** (Scheme 5). These catalysts have been shown to give high conversions at loadings as low as 0.05 mol % in self- and cross-metathesis reactions of fatty acid derivatives.[42] Moreover, the addition of 1 mol % of *p*-benzoquinone to these reactions efficiently prevents double bond isomerization,[49] which can drastically decrease the yield of the desired product.[42] Initially, catalyst loadings of 0.5 mol % were used, and the reactions were followed by GC-MS in order to identify the most active catalyst. Vacuum (200 mbar) was applied throughout the reaction to remove the released ethylene. Fast conversions were observed for all three catalysts within the first hour of reaction; however, the conversions did not further increase appreciably. **C1** gave the lowest conversion (48.12% after 5 h) with very low double bond isomerization (1.3%). **C2** and **C3** performed similarly leading to conversions over 80% with only slightly higher isomerization degrees around 2.5% after 5 h reaction. On the basis of these results, **C2** was selected for further optimization. Thus, **C2** loadings of 0.2 and 1 mol % were also tested; however, using 0.2 mol % resulted in lower conversion after 5 h reaction, and using 1 mol % gave a higher isomerization degree despite an increase in conversion. From these results, we could conclude that around 0.5 mol % **C2** is a suitable choice for the self-metathesis of **29**. The deprotection of the hydroxyl groups was carried out by direct reaction of the metathesis reaction mixture with excess of methanol in presence of TBD at 65 °C, and the product (**26**) was purified by recrystallization from methanol. It is worth to highlight the simplicity of this synthetic route, which leads to **26** with an overall yield of 67%, without chromatographic purification steps (Scheme 5).

The polymerizations of limonene-based monomers **16**−**19** were then performed with **24**, **25**, **26**, **27**, and **28** as fatty acid-based comonomers, in the presence of 5 mol % of TBD, and under continuous vacuum (10 mbar), leading to polyesters **P5**−**P14** (Scheme 6). Table 4 summarizes the results of these polymerizations at 120 °C for 7 h (data of precipitated polymers), and Figure 3 shows GPC traces of the (*R*)-(+)-limonene-derived polyesters for comparison. As expected, higher molecular weight polymers (between 9 and 24 kDa and PDI between 1.75 and 2.47) could be obtained in all cases. This was further confirmed by NMR analysis. As a representative example, Figure 4 shows the ^{1}H NMR spectra of diester **17** and **P5**, revealing the transformation of methyl ester (H^a) to the backbone ester links (H^c).

When short-chain comonomers are used, the activity of the catalyst can be reduced due to the steric hindrance caused by the terpene rings. On the other hand, the introduction of long, flexible alkyl chains can reduce the steric hindrance around the terpene units, facilitating the approach of the catalyst. Interestingly, when comparing the polymerization results obtained with diesters **24** (unsaturated, **P7**, and **P8**) and **28** (saturated, **P13**, and **P14**), higher molecular weights are obtained with the unsaturated diester, probably due to a more flexible chain both in the monomers and the resulting polymer.

Furthermore, a closer look at the polymerization results reveals an interesting fact regarding the obtained molecular weights. The molecular weights reached with diester monomers containing the methyl thioglycolate moiety (**17** and **19**) are clearly higher than those obtained with diesters which do not have the sulfur in *β*-position to the carbonyl group (**24** and **25**).

Scheme 6. Synthesis of (*R*)-(+)- and (*S*)-(−)-Limonene/Fatty Acid-Based Polyesters

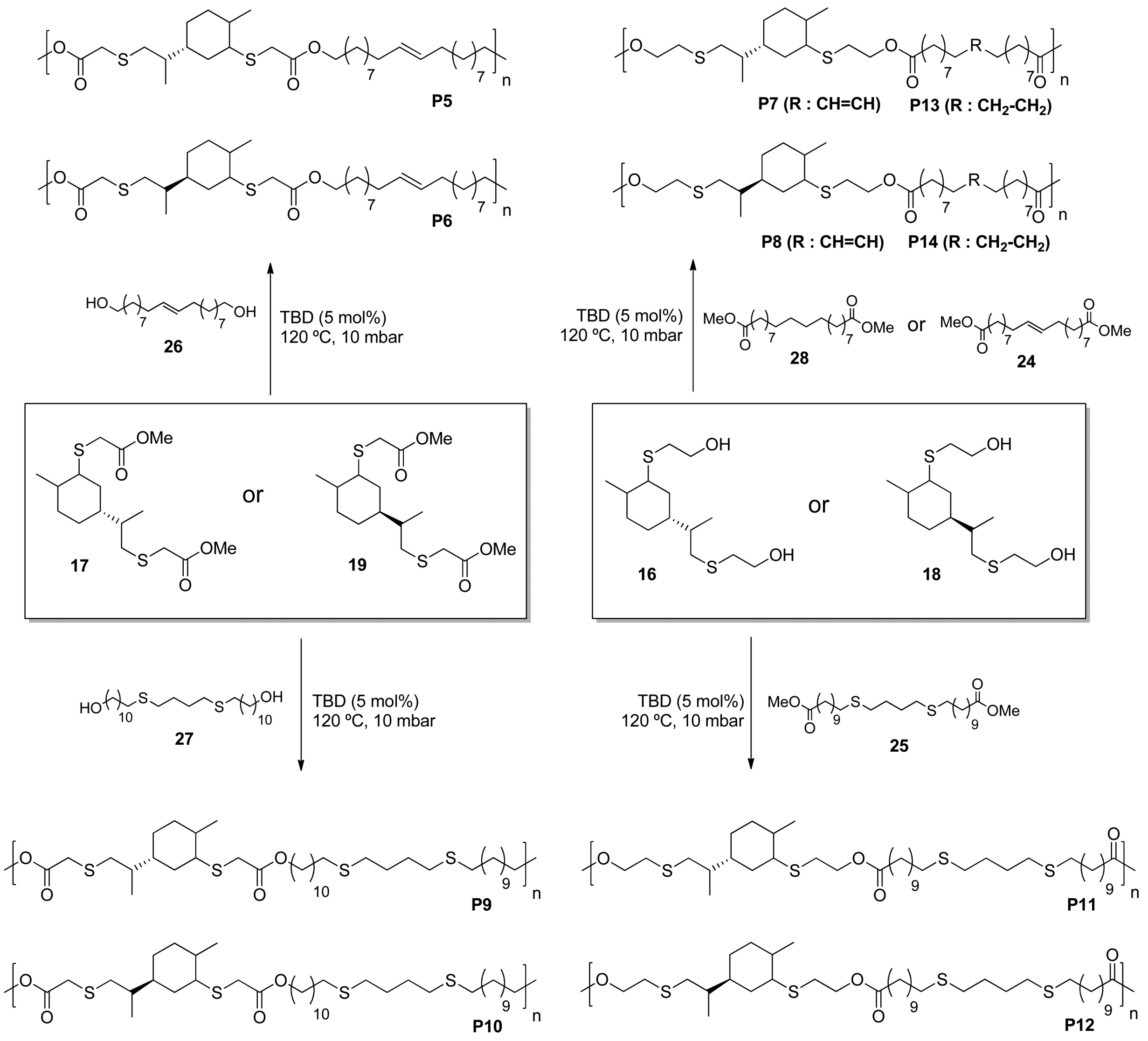


Table 4. Analytical Data of Synthesized (*R*)- and (*S*)-Limonene/Fatty Acid-Based Polyesters

polymer (diester/diol)	M_n[a] (kDa)	PDI[a]	T_g (°C)[b]/T_m (°C)[b]
P5 (**17**/**26**)	18.9	1.97	−46.9[c]/−15.4[c]
P6 (**19**/**26**)	21.3	2.00	−47.8[c]/−15.6[c]
P7 (**24**/**16**)	15.3	1.82	−46.6[d]/17.1[d]
P8 (**24**/**18**)	15.5	1.75	−45.3[e]/17.0[e]
P9 (**17**/**27**)	24.7	2.47	−45.4[f]/28.2[f]
P10 (**19**/**27**)	23.1	2.47	−46.3[d]/28.3[d]
P11 (**25**/**16**)	12.4	2.40	−41.9[d]/47.5[d]
P12 (**25**/**18**)	14.0	2.06	−43.0[g]/47.2[g]
P13 (**28**/**16**)	9.7	2.22	[h]/50.8[d]
P14 (**28**/**18**)	9.2	2.22	[h]/50.3[d]

[a] GPC data of precipitated polymers. [b] DSC data recorded at 10 °C/min. [c] 1 h annealing at −25 °C. [d] Second heating scan. [e] 1 h annealing at 16 °C. [f] 1 h annealing at 20 °C. [g] 1 h annealing at 10 °C. [h] T_g not observable by DSC.

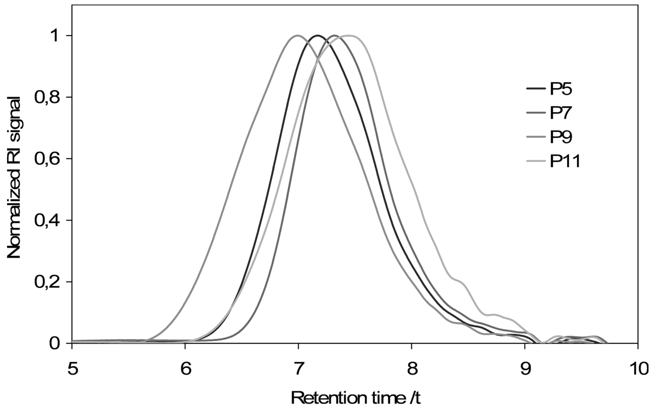


Figure 3. GPC traces of (*R*)-(+)-limonene-based polyesters.

In order to establish whether the sulfur atom has an effect on the course of the esterification reaction, we performed a simple

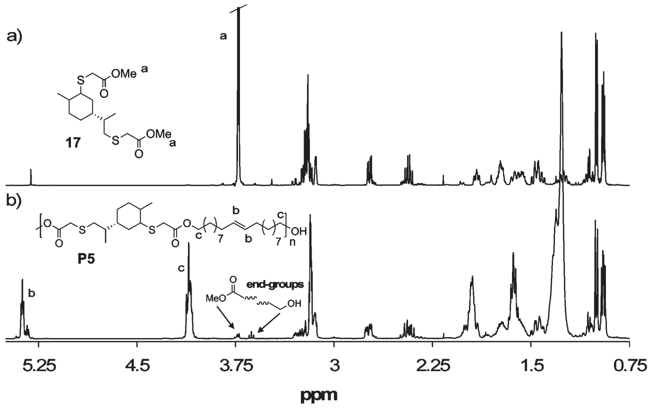


Figure 4. ^{1}H NMR spectra of (a) monomer **17** and (b) product of polycondensation of **17** with diol **26** (**P5**).

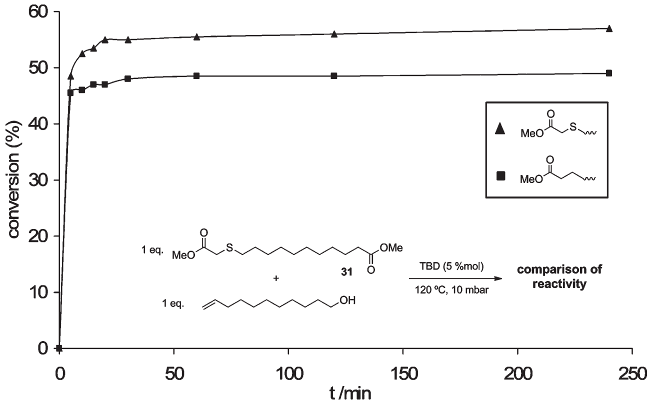


Figure 5. Study of the effect of sulfur in β-position to ester group on the reactivity toward transesterification with 10-undecen-1-ol.

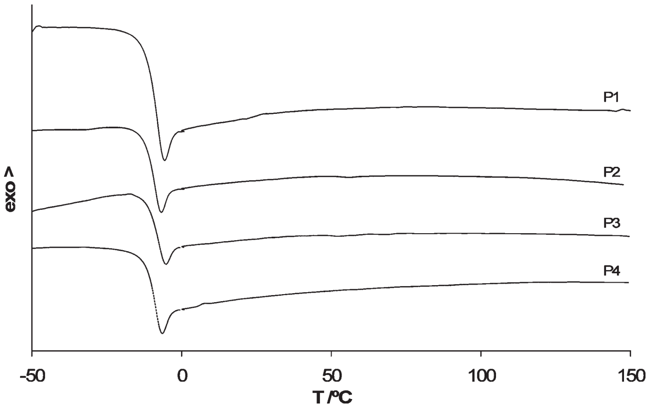


Figure 6. DSC traces of terpene-based polyesters **P1**−**P4** (second heating scan).

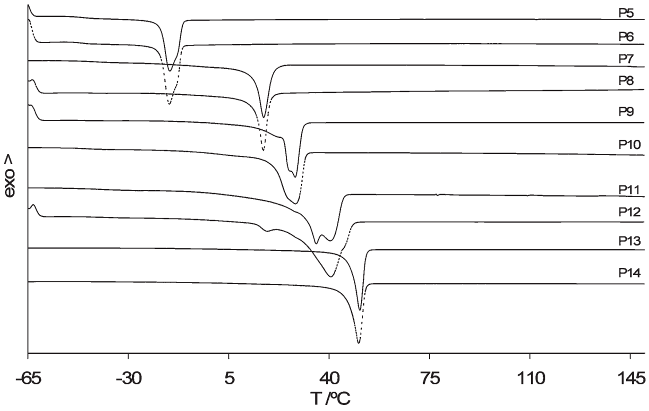


Figure 7. DSC traces of (*R*)-(+)-limonene (—) and (*S*)-(−)-limonene (···) based polyesters **P5**−**P14** (see Table 4 for experimental conditions).

kinetic study in which 10-undecen-1-ol was reacted with diester (**31**) containing both a methyl β-thioester and a methyl ester (Figure 5). The reaction was performed under polymerization conditions (5 mol % TBD related to ester groups, 120 °C, and 10 mbar) with a 1:1 molar ratio of the reactants, and the consumption of both ester groups was monitored in time by integration of characteristic ^{1}H NMR signals (see Supporting Information for details). The results of this competitive study, which are shown in Figure 5 as a plot of ester conversion against time, confirm the higher reactivity of the methyl β-thioester compared to the unsubstituted one.

The effect of sulfur on the reactivity of the ester group might be explained on the basis of the mechanism through which TBD catalyzes transesterification reactions. It has been proposed that in a first step a reversible amidation occurs by formation of a six-membered ring intermediate between TBD and the ester group followed by release of methanol.[50] In a second step, a hydrogen bond is established between the TBD moiety and the approaching alcohol, favoring its approach and weakening the O−H bond. In this second step, the sulfur atom might establish a hydrogen bond with the alcohol, thus assisting the process. This and other hypotheses are currently under investigation in order to clarify the role of sulfur in this reaction.

Thermal Analysis. Polyesters obtained from limonene-based monomers **20**−**23** (**P1**−**P4**) consist of bulky 1,3,6-trisubstituted cyclohexane units connected by very short segments. Crystallization is thus very unlikely, and DSC analysis reveals amorphous structures for all of them (see Figure 6) with glass transition temperatures around −10 °C.

Limonene/fatty acid-based polyesters **P5**−**P14** (Scheme 6) display as a common structural feature the alternation of relatively long aliphatic segments (18 and 20 carbon atoms) and substituted cycloalkanes. On one hand, the aliphatic chains are able to crystallize, but on the other hand, the 1,3,6-trisubstituted cyclohexane units are too bulky to crystallize. DSC traces obtained for polyesters **P5**−**P12** are shown in Figure 7, and the extracted analytical data are summarized in Table 4. With the exception of **P7**, **P10**, **P13**, and **P14**, the studied polyesters displayed multiple melting transitions on the second heating scan. Annealing studies were thus performed to determine whether these multiple melting transitions were due to the presence of metastable crystalline phases or actual crystalline structures (see Table 4 for experimental details). Appropriate annealing conditions could be found for **P5**, **P6**, **P8**, and **P12**, which led to one, more or less broad, melting peak. However, annealing studies performed on **P9** and **P11** did not lead to single melting transitions, suggesting polymorphism. A first look at the thermal data in Table 4 reveals that all the studied polyesters are semicrystalline, displaying both glass transition (T_g) and melting (T_m). Especially noteworthy is the fact that all studied polyesters (except **P13** and **P14**, for which the T_g could not be observed by

DSC) have basically the same glass transition temperature despite their clearly differentiated T_m values. This data could suggest that the polyester chains might crystallize independently of the cyclic moieties (common in all polyesters), letting them out of the crystallites as amorphous regions. The melting behavior of polyesters **P5**−**P14** can be explained attending to the factors that enhance or hinder interchain interactions and to their different chain-packing abilities. **P5** (T_m = −15.4 °C) and **P7** (T_m = 17.1 °C) present well-differentiated melting points despite having relatively similar structures. Both present bulky main-chain groups that can impede crystallization, but in this case, the spacing between the ester groups and the bulky limonene rings, which is longer in **P7**, seems to favor interchain interactions and/or chain packing compared to **P5**. The same applies for the pairs **P6**/**P8**, **P9**/**P11**, and **P10**/**P12**. On the other hand, the introduction of fatty acid-based comonomers containing sulfur atoms leads to an increase of the melting temperatures. Thus, polyesters **P9**−**P12** display melting temperatures which are up to 43 °C higher than for polyesters **P5**−**P8** (see e.g. **P5** vs **P9**). The effect of sulfur on the T_m of these polyesters can be correlated with a higher cohesion energy due to stronger interchain interactions.[51] Finally, saturated polyesters **P13** and **P14** display sharp melting endotherms, which are around 35 °C higher than those of their unsaturated counterparts (**P7** and **P8**). This effect is due to the higher packing ability of the saturated alkyl chains and to the higher flexibility of the unsaturated ones, which results in the observed higher melting points. No glass transition could be detected for these polyesters, which also supports their higher crystallinity compared to **P7** and **P8**.

CONCLUSIONS

Addition of alcohol and ester functionalized thiols to terpenes takes place at room temperature in the absence of solvent and radical initiator. These reactions are regioselective and can thus be controlled to yield monofunctional, difunctional, or heterodifunctional monomers which are interesting renewable building blocks. Moreover, it was found that the addition of thiols to terpenes is also diastereoselective, reaching a ratio of 5:1 for this radical reaction in the addition of 2-mercaptoethanol to (−)-*β*-pinene. This effect was related to steric effects making hydrogen abstraction more favorable from one of both terpene faces. Difunctional monomers prepared from (*R*)-(+)-limonene (**1**) and (*S*)-(−)-limonene (**2**) have been subjected to polycondensation. Oligomers or low molecular weight polyesters were obtained when these terpene-based monomers were homopolymerized or copolymerized with short-chain diols. However, when long-chain fatty acid-based diesters and diols were used as comonomers, polyesters with number-average molecular weights up to 25 kDa (M_n) were obtained. Most polyesters synthesized are semicrystalline with a common T_g around −45 °C and melting points ranging from −15 to 50 °C.

ASSOCIATED CONTENT

S Supporting Information. Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: m.a.r.meier@kit.edu.

ACKNOWLEDGMENT

M.F. is thankful for a fellowship from the Indonesian Directorate General of Higher Education.

DEDICATION

Dedicated to Professor Christian Bruneau on the occasion of his 60th birthday.

REFERENCES

(1) Christensen, C. H.; Rass-Hansen, J.; Marsden, C. C.; Taarning, E.; Egeblad, K. *ChemSusChem* **2008**, *1*, 283–289.

(2) Metzger, J. O.; Eissen, M. *C. R. Chim.* **2004**, *7*, 569–581.

(3) Corma, A.; Iborra, S.; Velty, A. *Chem. Rev.* **2007**, *107*, 2411–2502.

(4) Speight, J. G. In *Chemical Process and Design Handbook*; McGraw-Hill: New York, 2002.

(5) Burdock, G. A. In *Fenaroli's Handbook of Flavour Ingredients*, 3rd ed.; CRC Press: Boca Raton, FL, 1995.

(6) Nonino, E. A. *Perfum. Flavor.* **1997**, *22*, 53–58.

(7) Kerton, F. M. In *Alternative Solvents for Green Chemistry*; Clark, J. H., Kraus, G. A., Eds.; RSC Green Chemistry: Cambridge, UK, 2009; p 109.

(8) Thomas, A. F.; Bessière, Y. *Nat. Prod. Rep.* **1989**, 291–309.

(9) Posner, T. *Chem. Ber.* **1905**, *38*, 646–657.

(10) Griesbaum, K. *Angew. Chem.* **1970**, *82*, 276–290.

(11) Walling, C.; Helmreich, W. *J. Am. Chem. Soc.* **1959**, *81*, 1144–1148.

(12) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004–2021.

(13) Hoyle, C. E.; Lee, T. Y.; Roper, T. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5301–5338.

(14) Killops, K. L.; Campos, L. M.; Hawker, C. J. *J. Am. Chem. Soc.* **2008**, *130*, 5062–5064.

(15) Marvel, C. S.; Olson, L. E. *J. Polym. Sci.* **1957**, *26*, 23–28.

(16) Tolstikov, G. A.; Kanzafarov, F. Y.; Sangalov, Y. A.; Dzhemilev, U. M. *Neftekhimiya* **1979**, *19*, 425–429.

(17) Tolstikov, G. A.; Kanzafarov, F. Y.; Dzhemilev, U. M.; Kantyukova, R. G.; Zelenova, L. M. *Zh. Org. Khim.* **1983**, *19*, 2075.

(18) Janes, J. F.; Marr, I. M.; Unwin, N.; Banthorpe, D. V.; Yusuf, A. *Flavour Fragr. J.* **1993**, *8*, 289–294.

(19) Silvestre, A. J. D.; Gandini, A. In *Monomers, Polymers and Composites from Renewable Resources*; Belgacem, M. N., Gandini, A., Eds.; Elsevier: Oxford, 2008; p 17.

(20) Xie, R.; Chu, L.-Y.; Deng, J.-G. *Chem. Soc. Rev.* **2008**, *37*, 1243–1263.

(21) Nakano, T.; Okamoto, Y. *Chem. Rev.* **2001**, *101*, 4013–4038.

(22) Verbiest, T.; Kauranen, M.; Persoons, A. *J. Mater. Chem.* **1999**, *9*, 2005–2012.

(23) Kane-Maguire, L. A. P.; Wallace, G. G. *Chem. Soc. Rev.* **2010**, *39*, 2545–2576.

(24) (a) Roberts, W. J.; Day, A. R. *J. Am. Chem. Soc.* **1950**, *72*, 1226–1230. (b) Barros, M. T.; Petrova, K. T.; Ramos, A. M. *Eur. J. Org. Chem.* **2007**, *8*, 1357–1363. (c) Martinez, F. *J. Polym. Sci., Part A: Polym. Chem.* **1984**, *22*, 673–677.

(25) Satoh, K.; Sugiyama, H.; Kamigaito, M. *Green Chem.* **2006**, *8*, 878–882.

(26) Lu, J.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 27–31.

(27) Ramos, A. M.; Lobo, L. S. *Macromol. Symp.* **1998**, *128*, 43–50.

(28) Li, A.-L.; Wang, Y.; Liang, H.; Lu, J. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 2376–2387.

(29) Satoh, K.; Matsuda, M.; Nagai, K.; Kamigaito, M. *J. Am. Chem. Soc.* **2010**, *132*, 10003–10005.

(30) Barros, M. T.; Petrova, K. T.; Ramos, A. M. *Eur. J. Org. Chem.* **2007**, *8*, 1357–1363.

(31) Sharma, S.; Srivastava, A. K. *Eur. Polym. J.* **2004**, *40*, 2235–2240.

(32) Sharma, S.; Srivastava, A. K. *J. Macromol. Sci., Pure Appl. Chem.* **2003**, *A40*, 593–603.

(33) Sharma, S.; Srivastava, A. K. *Polym. Plast. Technol. Eng.* **2003**, *42*, 485–502.

(34) Sharma, S.; Srivastava, A. K. *Des. Monomers Polym.* **2006**, *9*, 503–516.

(35) Aikins, J. A.; Williams, F. In *Ring-Opening Polymerization*; McGrath, J. E., Ed.; ACS Symp. Ser.; American Chemical Society: Washington, DC, 1985; Vol. 286, Chapter 24, p 335.

(36) Byrne, C. M.; Allen, S. D.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2004**, *126*, 11404–11405.

(37) Türünç, O.; Meier, M. A. R. *Macromol. Rapid Commun.* **2010**, *31*, 1822–1826.

(38) Schuchardt, U.; Sercheli, R.; Vargas, R. M. *J. Braz. Chem. Soc.* **1998**, *9*, 199–210.

(39) Okada, M.; Aoi, K.; Mizuno, W.; Ito, S. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1135–1140.

(40) Seebach, D.; Hungerbuhler, E.; Haef, R.; Schnurrenberger, P. *Synthesis* **1982**, 138–141.

(41) (a) Coullerez, G.; Lowe, C.; Pechy, P.; Kausch, H. H.; Hilborn, J. *J. Mater. Sci., Mater. Med.* **2000**, *11*, 505–510. (b) Hiltunen, K.; Seppala, J. V.; Harkonen, M. *Macromolecules* **1997**, *30*, 373–379.

(42) Djigoué, G. B.; Meier, M. A. R. *Appl. Catal., A* **2009**, *368*, 158–162.

(43) Blackwell, H. E.; O'Leary, D. J.; Chatterjee, A. K.; Washenfelder, R. A.; Bussmann, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 58–71.

(44) Schmidt, B.; Staude, L. *J. Organomet. Chem.* **2006**, *691*, 5218–5221.

(45) Schmidt, B. *Eur. J. Org. Chem.* **2004**, *9*, 1865–1880.

(46) Banti, D.; Mol, J. C. *J. Organomet. Chem.* **2004**, *689*, 3113–3116.

(47) Lantelme, B.; Dumon, M.; Mai, C.; Pascault, J. P. *J. Non-Cryst. Solids* **1996**, *194*, 63–71.

(48) Rybak, A.; Meier, M. A. R. *Green Chem.* **2008**, *10*, 1099–1104.

(49) Hong, S. H.; Sanders, D. P.; Lee, C. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2005**, *127*, 17160–17161.

(50) Coles, M. P. *Chem. Commun.* **2009**, 3659–3676.

(51) Yoda, N. *J. Polym. Sci., Part A: Gen. Pap.* **1963**, *1*, 1323–1338.