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Modified Poly(ε-caprolactone)s: An Efficient and Renewable Access via Thia-Michael Addition and Baeyer–Villiger Oxidation

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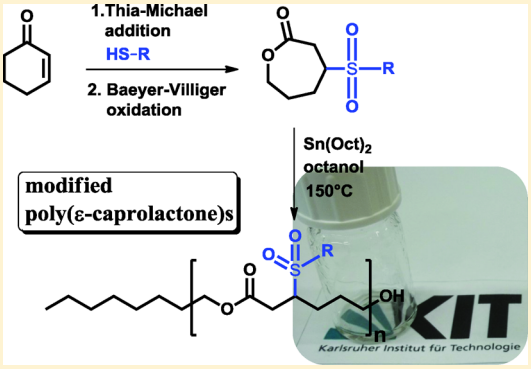
Supporting Information

ABSTRACT: The preparation of a novel class of ε-caprolactone (CL) monomers, modified at the β-position of the ester function, is described. The efficient thia-Michael addition to cyclohex-2-en-1-one and subsequent Baeyer–Villiger oxidation provided the regioselectively modified CL monomers. To enable a sustainable Baeyer–Villiger oxidation, several reaction procedures were investigated. In order to test a controlled ring-opening polymerization of the prepared monomers, the kinetics were studied and the monomer to initiator ratios were varied in order to prepare poly(ε-caprolactone)s with different molecular weights and different side groups.



INTRODUCTION

Aliphatic polyesters are a class of interesting polymeric materials. In particular, biodegradable and biocompatible aliphatic polyesters are highly attractive and valuable biomaterials, which can be used in a wide range of different applications.[1−7] Lactones and lactides are especially important monomers used to prepare versatile aliphatic polyesters with predictable molecular weights, narrow dispersities, and well-defined end-groups. Among different polymerization techniques, the controlled ring-opening polymerization utilizing diverse catalysts is most widely applied.[8] In order to promote a controlled ring-opening polymerization of lactones or lactides, a wide range of catalyst/initiators can be used, while tin and aluminum alkoxides are most frequently applied.[8] Considered as environmentally friendly and valuable thermoplastics, polycaprolactones (PCLs) have gained much interest since they can be functionalized and tailored for special applications in a straightforward manner.[9−12] Because of its biodegradability and biocompatibility, PCL is of great interests for tissue engineering and drug delivery applications.[7] Especially, PCL is an excellent material for tissue engineering since it is of nontoxic nature and revealed to be cyto-compatible with diverse body tissues.[7,13] Moreover, PCL can be used as drug carrier enabling a homogeneous drug distribution and long-term drug release.[14,15]

Industrially, the CL monomer is prepared by Baeyer–Villiger oxidation of cyclohexanone using peracetic acid, whereas for lab scale synthesis of CL monomers preferentially *m*-chloroperbenzoic acid (*m*CPBA) is used as oxidant.[16,17] Organic peracids are usually not environmentally benign and are shock sensitive, and the reactions are preferably carried out in chlorinated solvents. Thus, green alternatives and environmentally benign oxidation procedures making use of, e.g., diverse metal or enzyme catalysts and hydrogen peroxide as clean oxidant or potassium peroxymonosulfate ($KHSO_5$) as green oxidant are of great interest for the synthesis of the desired CL monomers.

Besides the development of greener and more efficient Baeyer–Villiger oxidation procedures there is a great interest in CL monomers from renewable resources. In a very interesting contribution by Heeres et al., the synthesis of CL was achieved by catalytic transformation of 5-hydroxymethylfurfural, which can be obtained from, e.g., D-fructose, starch, or cellulose.[18] Hillmyer and colleagues described the synthesis of diverse CL monomers from carvone or menthol.[19,20] Interestingly, the use of these renewable monomers enabled the synthesis of functional PCLs with different material properties.

Generally, the attachment of functional groups along the aliphatic chain of PCL (and other polymers) is highly attractive in order to tailor important material properties such as crystallinity, hydrophilicity, biodegradability, bioadhesion, and mechanical properties. Furthermore, pendent functional groups allow for a covalent attachment of molecules or probes of biological interest.[9] One common and important approach is to directly attach pendent functional groups (e.g., initiators, acrylates, alkynes, or halogens) to the lactone ring.[21,22] However, usually multistep synthesis procedures and extensive purification steps are needed to obtain the desired pure monomers.

Considering the importance of functionalized PCLs and the demand of CL monomers from renewable resources, we

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searched for a very efficient and straightforward approach to synthesize functionalized CL monomers, which can be derived from renewable resources. Therefore, the efficient thia-Michael addition to cyclohex-2-en-1-one is presented as universal approach to synthesize functionalized CL precursors. A subsequent Baeyer–Villiger oxidation of the cyclohexanone derivatives was used to prepare the corresponding functionalized CL monomers in a highly regio-selectivity manner.

RESULTS AND DISCUSSION

One aspect of this work was to synthesize the desired CL monomers from renewable resources. In the range of renewable resources given by nature, plant oils appeared to be very useful substrates to produce a variety of valuable chemicals.[23] The use of olefin metathesis appeared to be a very interesting oleochemical process to transform plant oils into valuable chemicals.[23] If polyunsaturated fatty acid derivatives are used for self-metathesis reactions, an intramolecular ring closing metathesis (RCM) to form 1,4-cyclohexadiene (CHD) as a byproduct occurs.[24] Our group also reported the self-metathesis of polyunsaturated fatty acid methyl esters to prepare long-chain diesters, wherein CHD is obtained as a byproduct (Figure 1).[25] Moreover, the group of Cole-Hamilton reported the

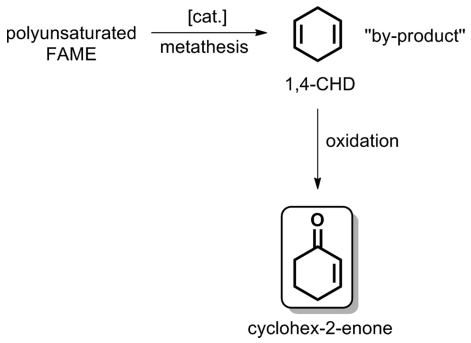

Figure 1. Generation of 1,4-cyclohexadiene (CHD) as byproduct of the olefin metathesis of polyunsaturated fatty acid methyl esters (FAMEs) and preparation of cyclohex-2-en-1-one from 1,4-CHD.

metathesis of cardanol with ethylene, also yielding CHD as a byproduct.[26] The described synthetic procedures offer a green alternative to the conventionally produced CHD from fossil resources. In particular, the valorization of CHD as byproduct is beneficial in a biorefinary concept, where all products of a feedstock should be utilized.

CHD cannot be directly converted to the desired modified CL monomers. A possibility to synthesize CL monomers is the Baeyer–Villiger oxidation of cyclohexanones. In order to prepare chemically modified CL, we thus used cyclohex-2-en-1-one as key substrate for Michael additions (Figure 1). Interestingly, cyclohex-2-en-1-one can be obtained from CHD in a sustainable way by selective two-phase hydrogenation and subsequent oxidation or direct liquid-phase oxidation of CHD.[27−30] As these reactions are described in the literature in detail, we did not further investigate this transformation and directly used commercially available cyclohex-2-en-1-one as starting material. Cyclohex-2-en-1-one is an ideal substrate for efficient Michael addition reactions. The reaction of such enones with thiols is also classified as click-reaction, allowing for an equimolar use of the reagents, enabling a very simple purification of the products by evaporation of the amine catalyst or washing with water, while preforming the reaction under mild and solvent-free conditions.[31]

Hence, we first used different thiols to prepare the cyclohexanones **1**–**4** by thia-Michael addition. To prepare the modified CL monomers **5**–**8**, the cyclohexanones **1**–**4** were subsequently transformed by Baeyer–Villiger oxidations. Thia-Michael additions were performed under solvent-free conditions using triethylamine as catalyst. Full conversion of the substrates was observed by GC–MS after 16h at 30 °C. The obtained products were purified by simply applying high-vacuum to remove the catalyst.

Without further purification steps, the cyclohexanone derivatives were used in Baeyer–Villiger oxidations to prepare the desired monomers (Figure 2). For the Baeyer–Villiger

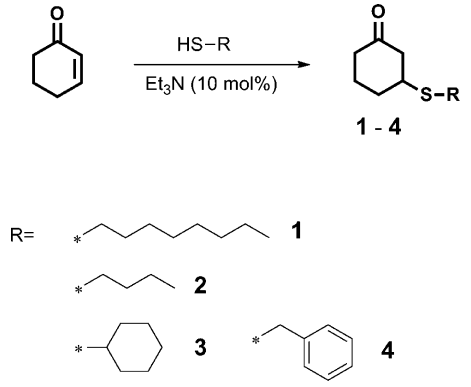

Figure 2. Thia-Michael addition of cyloehex-2-enone using different thiols.

oxidations, we first used conventional reaction conditions, utilizing *m*CPBA as oxidant and dichloromethane as solvent in order to have the modified CL monomers in hands and to study their polymerization and material properties. Further studies of more sustainable Baeyer–Villiger procedures will be discussed below. It has to be noted that during the Baeyer–Villiger oxidation, the sulfide moiety was oxidized to the sulfone. Reaction studies utilizing *m*CPBA as oxidant revealed that the oxidation of the ketone and the sulfide proceed simultaneously. Therefore, to ensure full oxidation of the sulfide to the sulfone and the oxidation of the ketone to the ester an excess of *m*CPBA was used (see also the experimental part in the Supporting Information). Using ice bath cooling, *m*CPBA was added and full conversion was observed after stirring the reaction mixture for 24 h at room temperature. The desired monomers could be isolated in yields up to 85%. Very interestingly, detailed NMR analysis revealed the formation of only one regio-isomer, namely 3-(substituted-sulfonyl)-ε-caprolactone, during the Baeyer–Villiger oxidation allowing the preparation of well-defined modified PCLs (see Supporting Information). Generally, the synthetic strategy using cyclohex-2-en-1-one as an efficient Michael acceptor to prepare modified cyclohexanones as CL precursors and subsequent monomer synthesis by Baeyer–Villiger oxidations is of outstanding simplicity (Figure 3). Interestingly, the functionalization at the β-position of CL is rarely described, which will lead to a novel class of modified CL monomers having sulfonyl moieties for the preparation of poly(3-sulfonyl-ε-caprolactone)s.

To enable a more sustainable Baeyer–Villiger oxidation of the cyclohexanone derivatives, we studied several alternative oxidation procedures (Table 1). It has to be noted that the

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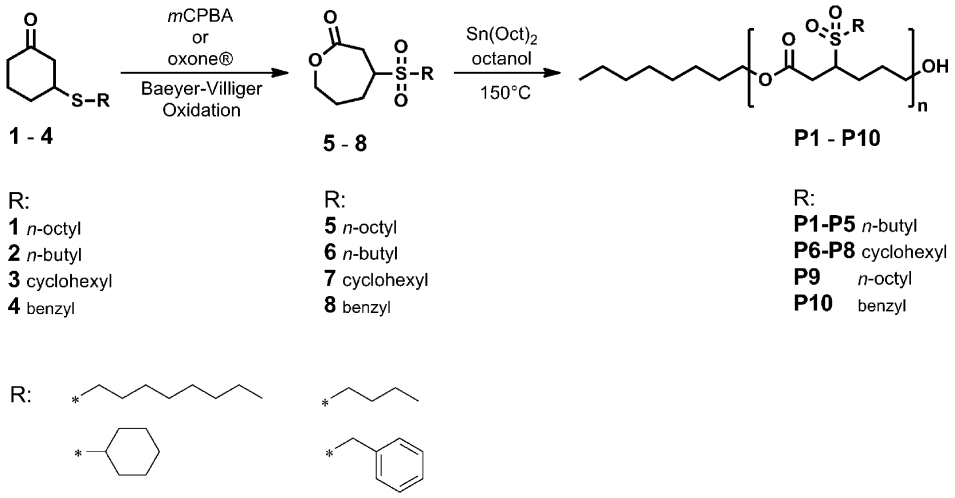

Figure 3. Baeyer–Villiger oxidation of the cyclohexanone substrates **1**–**4** and the ring-opening polymerization of the ε-caprolactone monomers **5**–**8**.

Table 1. Results Obtained from the Different Baeyer–Villiger Oxidation Procedures

procedure	conversion [%][a]	yield [%][b]
A (Novozyme 435/ethyl acetate)	≤10	n.d.
B (Novozyme 435/octanoic acid)	~5	n.d.
C (urea hydrogen peroxide/TFAA)	100	n.d.
D (oxone)	100	55–70
E (mCPBA)	100	77–85

[a]Determined via GC-MS. [b]Isolated yield, n.d. = not determined.

Baeyer–Villiger oxidation should be performed under mild reaction conditions to avoid an elimination of the sulfide (more precisely the intermediately formed sulfoxide). At first, with regard to a reaction optimization, the produced *m*-chlorobenzoic acid was isolated from the crude reaction mixture in order to enable a recycling of the used *m*CPBA as already described by, e.g., Jain and co-workers.[32]

In Baeyer–Villiger oxidations using octanoic acid (Table 1, entry A) or ethyl acetate (entry B) as peracid source and Novozyme 435 as catalyst, only low conversions were obtained after a reaction time of 7 days. Thus, contrary to the conversion of, e.g., cyclohexanone to CL via Novozyme 435 catalyzed Baeyer–Villiger oxidation,[33,34] the thiol functionalized substrates are seemed incompatible with the enzyme catalyst and/or the applied reaction conditions. Baeyer–Villiger oxidations preformed with urea hydrogen peroxide as oxidant as reported by Mecking and co-workers[35] yielded full conversions of the substrates, but low yields and regio-selectivity were obtained (entry C). Most promising, the utilization of oxone as green oxidant for Baeyer–Villiger oxidations, as, e.g., described by Hillmyer et al.,[19] yielded full conversion of the substrates performing the reaction at room temperature (entry D). Thereby, the utilized solvent is of crucial importance. In oxidation reactions performed in dichloromethane or methanol/water, low yields were obtained. However, if the reaction was performed in *N*,*N*-dimethylformamide full conversion and yields up to 70% were achieved. Although the conventionally performed Baeyer–Villiger oxidation afforded higher yields, the applied procedure making use of oxone appeared to be a promising green alternative.

Subsequently, the prepared CL monomers were studied in ring-opening polymerizations. Because of the poor solubility of the monomers, the best results were obtained if the polymerizations were performed at 150 °C under solvent-free conditions using tin(II)octanoate as catalyst and 1-octanol as initiator (Figure 3). The kinetics of the polymerization were studied by SEC analysis by monitoring the monomer conversion (Figure 4).

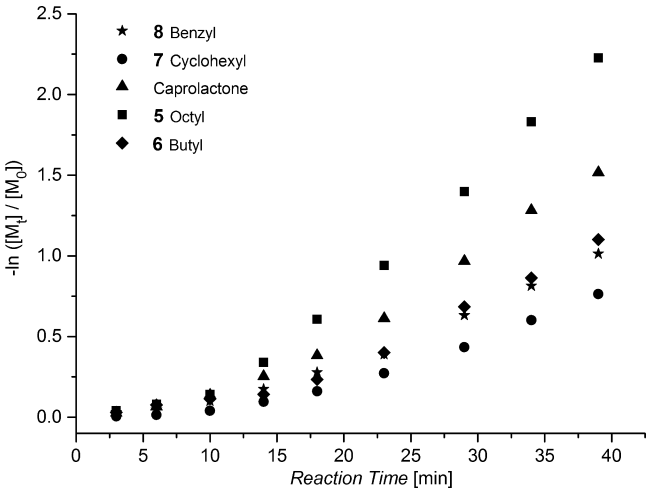

Figure 4. Kinetic studies of the ring-opening polymerization of the modified caprolactone monomers **5**–**8** and CL.

Compared to CL, the polymerizations of the modified CLs proceeded slower, except for monomer **5** having the *n*-octylsulfonyl moiety. Although **5** seemed to be sterically more hindered than monomer **6**, the polymerization was significantly faster (Figure 4). This might be due to a difference of the viscosity of the reaction mixture containing the monomer and growing polymer, resulting in different diffusion coefficients. This assumption is supported by the result of the kinetic measurement of monomer **7** having a cyclohexylsulfonyl moiety. Monomer **7** displayed the highest melting point (136 °C) and the polymerization mixture was hardly stirrable after 45 min of reaction time, resulting in a slower polymerization rate. However, the kinetic measurements revealed a living character of all performed ring-opening polymerizations (linear correlation of $-\ln([M_t]/[M_0])$ vs reaction time and M_n vs conversion; Figure 4 and Figure S30 in the Supporting

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Information). It has to be noted that the polymerization displayed a short induction time, but in this time range, the determination of the monomer conversion was difficult by SEC due to overlapping peaks. It should also be noted here that a determination of conversions by NMR and/or GC was not possible due to indistinguishable peaks in NMR and impossible detection of the monomers in GC.

It should be also noted that the molecular weights determined by SEC analysis differ from the theoretically expected values due to an inaccuracy of SEC analysis since the prepared polyesters with the sulfonyl moieties are very different to the PMMA standards used for the calibration. However, the SEC analysis of all polyesters revealed polymers with narrow dispersities of 1.10−1.28 and homogeneous molecular weight distributions (Figure 5, Table 1 and 2). **P4** and **P5** showed

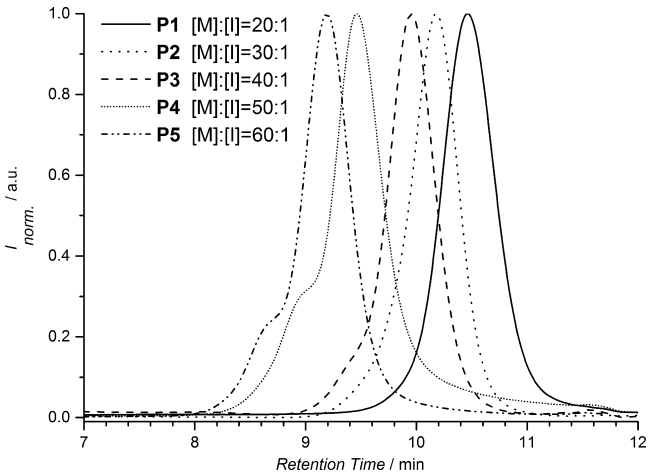

Figure 5. SEC analysis of the polyesters **P1**−**P5** prepared from monomer **6** using different monomer to initiator ratios.

Table 2. Results of the SEC Analysis of the Prepared Polyesters P1−P5 Using Monomer 6 and Different Monomer to Initiator ([M]/[I]) Ratios

polymer	[M]/[I]	$M_{n,theo}$ [Da]	$M_{n,SEC}$ [Da]	$Đ$
P1	20:1	4812	2740	1.28
P2	30:1	7153	6320	1.13
P3	40:1	9494	7400	1.10
P4	50:1	11 835	12 540	1.16
P5	60:1	14 176	18 420	1.17

small shoulders at higher molecular weights, which can be explained by a slow intermolecular transesterification process occurring after complete conversion.[20,36,37] For further studies (*n*-butylsulfonyl)cyclohexane was used to investigate the stability of the sulfone moiety (see Supporting Information). The results demonstrated that the sulfone is stable under the applied polymerization conditions and no side reactions occurred. Moreover, ^{1}H NMR analysis of the crude and precipitated polymers revealed defined polyesters without the occurrence of side reactions, such as elimination, also demonstrating the compatibility of the monomers with the applied polymerization conditions.

By varying the monomer to initiator ratio, the molecular weight of the polymers could be well adjusted, also clearly demonstrating a good control of the ring-opening polymerization (Figure 5, Table 1; see also Supporting Information).

The resulting polyesters were obtained as transparent materials in nearly quantitative yields after a reprecipitation and their thermal properties were studied by DSC analysis. All polyesters containing the sulfonyl moieties displayed no melt transitions and no thermal degradation up to 180 °C. In contrast to conventional CL, the sterically demanding sulfonyl moieties prevent interactions of the polymer chains and formation of crystalline segments. The DSC measurements showed glass transition temperatures of the polyesters between 0−52 °C (Table 2). Polymer **P10** showed the highest T_g with 52 °C, whereas polymer **P9** having a long dangling side chain showed the lowest T_g of 0 °C. Generally, the T_g decreases with a longer dangling sulfonyl moiety, which prevents chain−chain interactions. In case of **P10** the polymer shows a higher T_g than the other polymers due to increased chain interaction by $\pi-\pi$ interaction of the aromatic moiety. The obtained results prove the successful use of the modified CL monomers for the preparation of defined polyesters with narrow dispersities and varying pendent side groups.

Table 3. Results of the SEC and DSC Analysis of the Polyesters P3, P8−P10 Using a Monomer to Initiator Ratio of [M]/[I] = 40:1

polymer	$M_{n,SEC}$ [Da]	$Đ$	T_g [°C]
P3 (*n*-butyl)	7400	1.10	7
P8 (cyclohexyl)	7680	1.17	40
P9 (*n*-octyl)	8840	1.12	0
P10 (benzyl)	6100	1.15	52

Depending on the thiol used in the thia-Michael reaction to modify cyclohex-2-en-1-one, the thermal properties of the corresponding polyester are significantly different. Moreover, the presented synthesis strategy offers an efficient and very straightforward possibility for the design of diverse modified CL monomers. Additionally, the method can be extended to other Michael donors making this strategy a universal approach to prepare versatile CL monomers and polyesters with novel material properties.

CONCLUSION

The preparation of a novel class of CL monomers modified with different sulfonyl moieties at the β-position of the carbonyl function is described. To achieve this, the thia-Michael addition to cyclohex-2-en-1-one is revealed to be an excellent strategy to prepare modified CL precursor since complete atom-efficiency, simple purification, and performance under very mild and solvent-free conditions makes this approach highly attractive. The modified CL monomers were prepared by Baeyer−Villiger oxidation of the cyclohexanone derivatives. As an alternative and more sustainable Baeyer−Villiger reaction procedure, the use of oxone as green oxidant revealed to be very promising. Interestingly, the performed Baeyer−Villiger oxidations are highly regioselective, allowing the synthesis of well-defined polyesters. The kinetics of the ring-opening polymerizations of the modified CL monomers were studied and compared to CL, revealing a controlled ring-opening polymerization of these novel monomers. Furthermore, by changing the monomer to initiator ratio, the molecular weights of the PCL bearing sulfonyl groups could be well adjusted. The resulting polymers were transparent and showed variable glass transitions depending on the sulfonyl moiety attached to the polyester. All in all, the presented synthetic strategy is of high simplicity

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and the desired modified CL monomers, which were used to prepare PCLs having different sulfonyl groups, are obtained in only two very straightforward and efficient synthesis steps.

■ ASSOCIATED CONTENT

Supporting Information

Detailed description of all experimental procedures and $^{1}H/^{13}C$ NMR and mass data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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