Optimization of the Property Profile of Poly-L-Lactide by Synthesis of PLLA-Polystyrene–Block Copolymers

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ABSTRACT: Diblock and triblock copolymers of poly-L-lactide (PLLA) and polystyrene (PS) were synthesized and the mechanical properties of these copolymers studied. Free radical polymerization of styrene in the presence of 2-mercaptoethanol as functional chain transfer agent produced mono-functionalized PS-blocks which were used as macroinitiators in the subsequent ring opening polymerization (ROP) of L-lactide to produce the diblock copolymers. Furthermore a α-ω-bishydroxyl functionalized PS-block was synthesized by RAFT, which was then engaged as bifunctional initiator for the ROP of L-lactide to provide the triblock copolymers PLLA-PS-PLLA. Through the copolymerisation and high molar masses, it was possible to achieve an improved mechanical property profile, compared with pure PLLA, or the analogous blends of PLLA and PS. A weight fraction of PS of 10–30% was found to be the optimal range for improving the heat deflection temperature (HDT), as well as mechanical properties such as ultimate tensile strength or elongation at break. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Poly (lactid acid) (PLA) has become much explored as emerging high volume polymer based on sustainable resources, by virtue of the availability of its monomer by fermentation from agricultural waste and its biodegradability.

PLA possesses several interesting material properties, which assure a high market potential for this "green" polymer, so far mostly in the packaging sector.[1] However, to open additional fields of application, it is necessary to improve its mechanical and thermical properties. Especially the low heat distortion temperature (HDT) of about 65°C prevents so far the use in many fields of applications.

A common way to improve the thermical properties is the synthesis of stereocomplexes of poly-D-lactide and poly-L-lactide.[2–6] Depending on the intended usage, these can have better mechanical properties compared with pure PLLA respectively PDLA. While L-lactide is easily produced through fermentation of starch today, the D-lactide for producing PDLA and the stereo complexes is not sufficiently available. Furthermore, high molar masses of PLLA are needed to provide good mechanical properties. But with increasing molar masses, the blends of PLLA and PDLA are inclined to phase segregation before they cocrystallize.

An alternative strategy to improve the properties of PLA, is the blending with other polymers,[7] i.e., the use of hybrids of bio-based and synthetic polymers. Although the properties of the main component can be improved in many cases by blending, in case of PLA, the reached effect is not sufficient for many applications.

With the intention to use renewable PLA on a large scale, it is important that the composite contains a high fraction of PLA.

Compared with physical blends, in which the polymers tend to segregate with increasing chain length and increasing difference of the solubility behaviour,[8] copolymers have the advantage, that the mixing of the components is inherent.

For instance, statistic copolymers of PLA are especially synthesized for medicinal applications. Lactide is copolymerized with glycolide or lactones[9,10] to adjust the properties like decomposition rate, hydrophilicity or elasticity. However, to achieve additive property profiles, graft, or even better block copolymers are needed. Up to now, most reported block copolymers consist of PLA and PEG.[11] Also diblock copolymers[12] as well as triblock copolymers[13,14] and multiblock copolymers of lactide, lactones, and PEG have been described.[15–18]
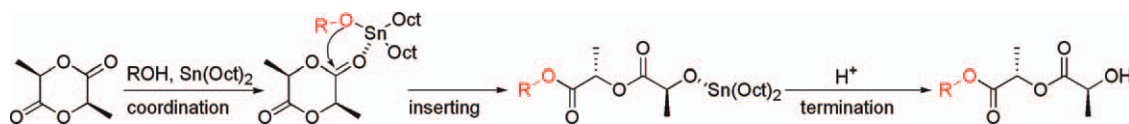
Scheme 1. Ring opening polymerization (ROP) of lactide initiated by hydroxyl group.

Polystyrene (PS) has advantages in its property profile. It is amorphous, transparent, and the glass transition temperature is above the boiling point of water. Therefore, combination of PLA and PS appears highly attractive.

Because PLA and PS are not compatible, it is of high interest to produce appropriate PLA-PS-block copolymers since the mechanical properties fall of in quality with increasing phase separation. Whereas several efforts towards block copolymers of PLA and PS have already been described,[19,20] the obtained copolymers have not been suitable to improve the mechanical properties of PLA, presumably due to their suboptimal composition and their relatively low molar masses. Thus, we have explored the effect of block copolymer composition and architecture on mechanical key parameters such as tensile strength or E-modulus.

Binary diblock and triblock copolymers were prepared by ROP of lactide on mono and di-α-ω-hydroxy functionalized PS macroinitiators, striving for higher molar masses and limited PS-fractions of 10 to 35wt% only. So the block copolymers have a high content of biobased component.

RESULTS AND DISCUSSION

Beside polycondensation the ROP is the main method to produce polylactide (Scheme 1).[21–23]

Block copolymerization was achieved by using end functionalized PS as macroinitiator. Monofunctional macroinitiators were prepared via free radical polymerization of styrene with VA-086 as hydroxyl functionalized azoinitiator **1** and mercaptoethanol **2** as hydroxyl functionalized chain transfer agent.[24] In this way, complete endgroup functionalization of the PS blocks was assured. Inevitably, a small percentage of the polystyrene blocks

gets difunctionalized by termination via recombination of the growing polymer chains. Still, when using a high molar ratio of chain transfer agent to initiator, these impurities are small (Figure 1).

Beside the diblock copolymers **DC**, being preparable as explained, there were also triblock copolymers **TC** prepared (Figure 2).

For preparing binary triblock copolymers **TC**, α-ω-bifunctional polystyrene was engaged in the ROP of lactide. The RAFT-method[25,26] (reversible addition fragmentation chain transfer polymerization) was used to prepare the bifunctionalized polystyrene block.

On the basis of the bifunctional RAFT agent[27] **3**, the sequence RAFT-polymerization, aminolysis,[28,29] and alkylation with bromoethanol[30] provided the required difunctional macroinitiator for the following ROP step (Scheme 2).

The direct use of thiol functionalized polystyrene as macroinitiator in the ROP of lactide is known.[31] However, the used hydroxyl ethylation chosen by us results in thioether and ester bonds, which both are thermally more stable than the thioester-moiety formed when using thiol initiators. The direct transformation of the thiol into the hydroxyl was described as alternative strategy,[32,33] but in doing so, the oxidative stress of this pathway may damage the polymer. In this way, block copolymers of PS and PLLA were prepared.

The selective dissolution of PS in toluene was used to verify the extent of block copolymer formation with PLLA. It was found by gravimetric analysis, that the produced material was virtually insoluble in toluene. Accordingly, the extend of block copolymer formation was > 90% for all samples.
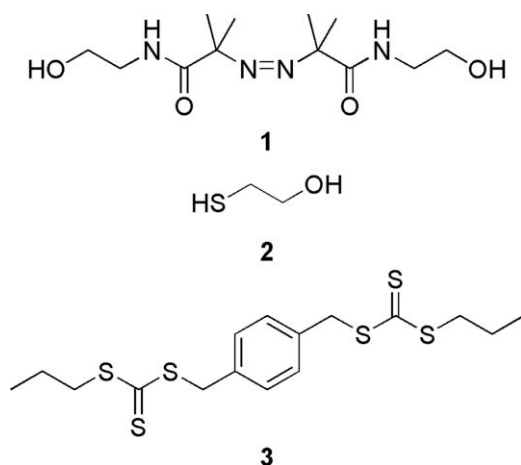
Figure 1. Additives of the syntheses.
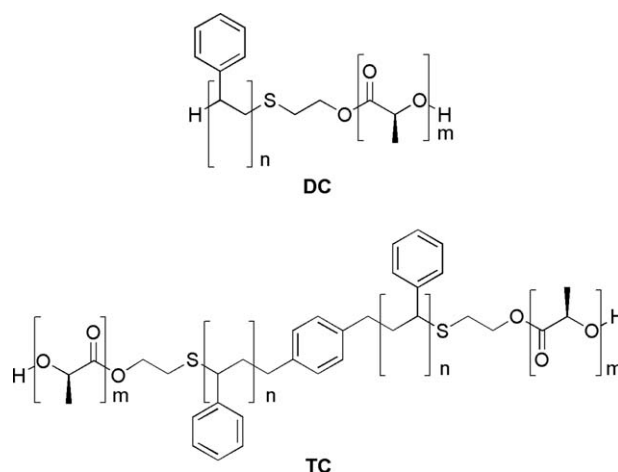
Figure 2. Prepared di- and triblock copolymers.
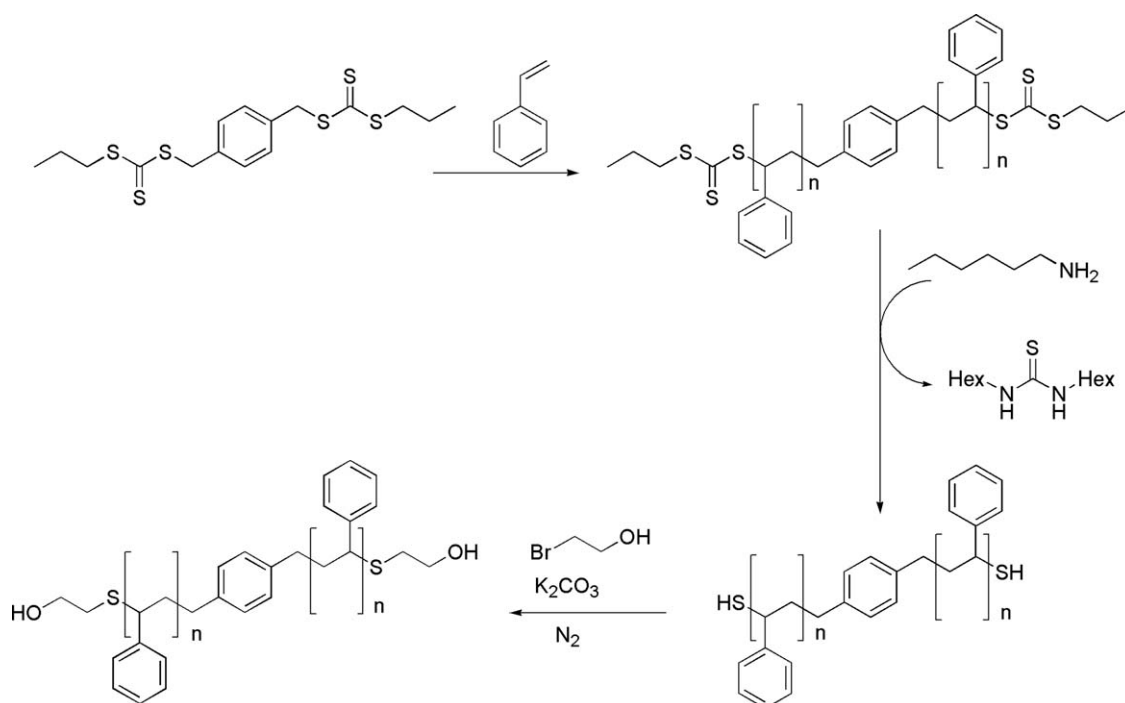
Scheme 2. Synthesis of the difunctionalized macroinitiator.

Blockcopolymer DC2a was analyzed using SEC with both UV- and RI-detection. The allocation of PS (UV) and blockcopolymer (RI) is an additional verification for block copolymer formation (Figure 3).

Key mechanical properties of the block copolymers were analyzed and compared with commercially available high molar mass PLLA, and the corresponding physical blends (Table I).

Comparing the data of **DC1** and **blend 1** or of **DC3** and **blend 3** in Table I or Figure 5 it reveal, that the HDT values of the blends and the block copolymers are very similar. Also the thermal degradation is similar (Figure 4).

However, Figure 6 shows, that the diblock copolymers have significantly increased mechanical strength compared to the physical blends.

Accordingly, the strategy of using block copolymers of PS and PLLA results indeed in materials with improved properties over pure PLLA or analogous blends.

Further, the improvement of the mechanical properties with increasing PS content is asymptotic. Small amounts of polystyrene as in copolymer **DC1** result in a strong improvement of the properties. A further increase of the fraction of PS to 35% as in **DC3**, leads only to a small additional increase of the HDT. However, the resulting mechanical properties are even somewhat inferior in comparison to **DC1** (Figures 5 and 6).

In addition to the variation of the fraction of polystyrene in the system, we varied the molar mass of the polystyrene macro initiators too, while keeping the fraction of polystyrene constant (DC 2a and 2b in Table I). It was found, that the lower molar mass of PS of about 30,000 g/mol yielded the better results.

It might be interesting to see the effect of even lower molar masses, but within the experimental set up chosen, this would not lead to meaningful results. For the given weight fraction of PS, the use of much shorter PS-chains as macroinitiators would imply much lower molar masses of the PLA block, too. However, it is known, that molar masses of about 70,000 g/mol are necessary for good mechanical properties of PLA.

In any case, it is evident from Table I and Figure 7, that the use of a higher molar mass of the macroinitiator results in similar mechanical properties, as shown by the comparison of copolymer DC2a and DC2b. The PS-macroinitiator of DC2b has a molar mass of 52,000 g/mol. Still, the resulting copolymer did not show any improvement compared to DC2a.
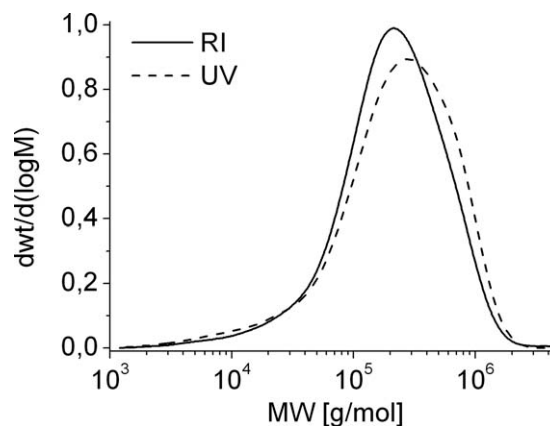
Figure 3. SEC-elugram of DC2a.

Table I. Comparison of Mechanical Properties and HDT of PLA 4042D, Selected Block Copolymers and the Accordant Blends after Annealing for 30 min with 115°C

Name	wt% PS:PLLA	M_n^a (PS)	M_n^b (PLLA)	M_n^a (copolymer)	δ_{max}^c (Mpa)	ε_{break} (%)	E-modulus (MPa)	HDT (°C)
PLLA (4042 D)	0 : 100	–	92,000	–	69	6	2,400	60
Blend 1	10 : 90	30,000	92,000	–	56	4	2,300	82
Blend 3	32 : 68	30,000	56,000	–	43	1.9	2,600	105
DC1	11 : 89	30,000	67,000	97,000	76.5	8	3,000	97
DC2a	23 : 77	30,000	48,000	78,000	71	4.2	2,800	107
DC2b	22 : 78	52,000	60,000	112,000	69	3.8	2,800	103
DC3	35 : 65	30,000	40,000	70,000	71	4.9	2,800	105
TC1	14 : 86	40,000	47,000	87,000	56	6	2,400	85
TC3	33 : 67	40,000	14,000	54,000	63	3.6	2,500	98

[a]Determined by SEC, [b]To facilitate the comparison of the data in Table I the molar masses of the PLLA-blocks of the copolymers are indicated. These are only calculated by the difference of the exactly known molar masses of the macro initiators, and the molar masses of the copolymers, [c]Ultimate tensile strength.

Consequently, a relatively small amount of PS is sufficient to optimize the mechanical properties of PS-PLLA block copolymers (Figure 7).

In addition to diblock copolymers, triblock copolymers PLLA-PS-PLLA **TC** were synthesized. The aim of these syntheses was to analyze, whether the mechanical properties can be improved by varying the architecture of the copolymers. As shown in Figure 8, the mechanical properties of the triblock copolymers are inferior to the ones of the diblock copolymers. This may be explained by the fact, that the polylactide is split into two relative small blocks, in order to have the same overall composition of the di- and triblock copolymers. These relative small blocks might disturb crystallization of the PLLA-chains (Figure 8).

EXPERIMENTAL
Materials
L,L-lactide (Uhde Inventa Fischer), was recrystallized from toluene, to reduce the content of titratable COOH-groups to 3ppm. Styrene (>99%, Sigma-Aldrich), β-mercaptoethanol (AppliChem), 2,2′Azobis[2-methyl-N-(2-hydroxyethyl)-propionamide](VA-086)-radical initiator (WAKO), toluene (>99.9%,

Merck), tin(II) 2-ethylhexanoate (∼ 95%, Sigma-Aldrich), 2-bromoethanol (95%, Sigma-Aldrich), hexylamine (99%, Sigma-Aldrich) were used as received. RAFT-agent **3** was a kind gift of Dr. Michael Päch. PLLA 4042D is a product of NatureWorks LLC.

Syntheses
Synthesis of the Macroinitiator M1 by Free Radical Polymerization. Totally, 400 mL (3.49 mol) freshly destilled styrene, 240 mL (2.27 mol) toluene, 400 μL (5.73 mmol) 2-mercaptoethanol and 0.4 g (1.39 mmol) VA-086 in 8 mL of methanol, are stirred in a three neck flask, while purging with nitrogen for 30 min. Subsequently the reaction mixture is heated to 92°C for 48 h under nitrogen blanket, whereby viscosity increases. The formed polystyrene is precipitated in 5 L of methanol and dried. Yield: 186 g (51.1%), white powder.

Synthesis of the Macroinitiator M2 by Free Radical Polymerization. Totally, 25 mL (0.218 mol) freshly destilled styrene, 15 mL toluene (0.142 mol), 15 μL (0.215 mmol) β-mercaptoethanol and 25 mg (0.087 mmol) VA-086 in 1 mL of methanol, are stirred in a three neck flask, while purging with nitrogen for 30 min. Subsequently the reaction mixture is
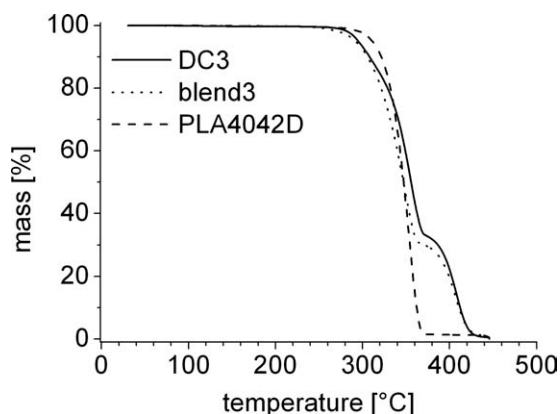
Figure 4. Comparison of the thermal degradation of DC3, blend 3, and PLA 4042D.
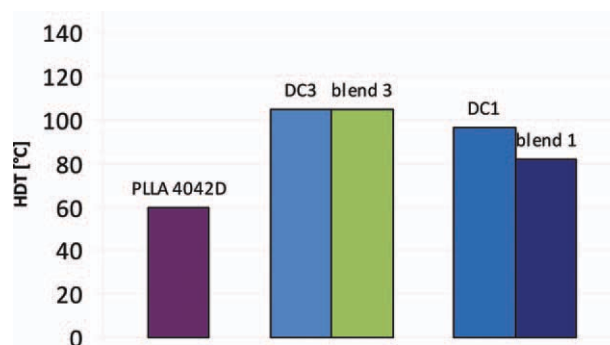
Figure 5. Comparison of the heat distortion temperature of DC1, DC3, the corresponding blends and PLA 4042D. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
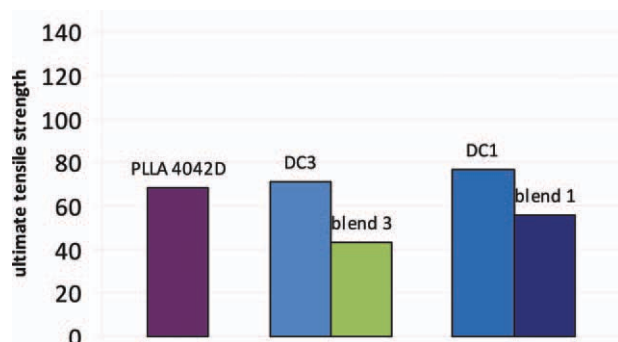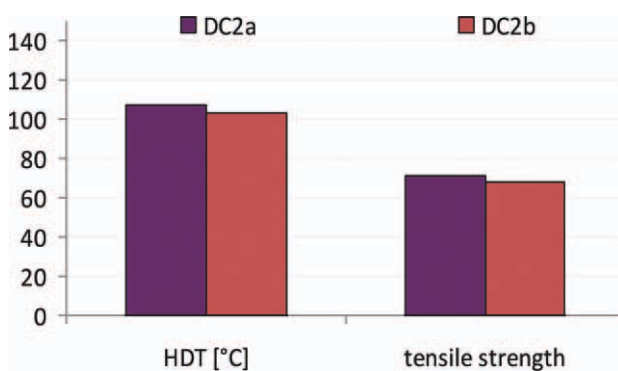
Figure 6. Comparison of the ultimate tensile strength of DC1, DC3, the corresponding blends and PLA 4042D. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8. Comparison of the heat distortion temperature and the ultimate tensile strength of diblock copolymers with analogous triblock copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

heated to 92°C for 48 h under nitrogen blanket, whereby viscosity increases. The formed polystyrene is precipitated in 300 mL of methanol and dried. Yield: 11.3 g (49.7%) white powder.
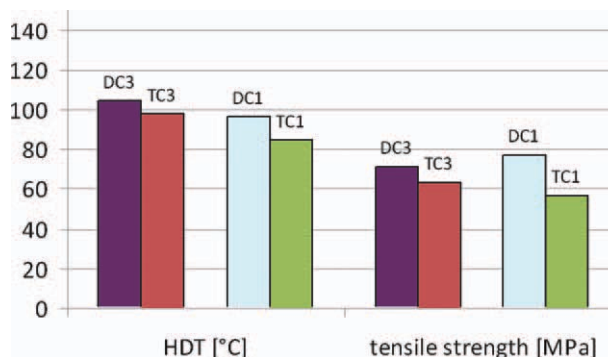
Synthesis of the Dihydroxyl Macroinitiator M3 by a RAFT Reaction. Step 1: 490 mL (4.28 mol) freshly destilled styrene and 3.08 g (7.59 mmol) of the intensive yellow RAFT-agent **3** are stirred at room temperature under a nitrogen blanket. After 1 h the reaction mixture is heated up to 110°C without adding an initiator. After 21 h the viscosity started to increase. 5 h later, the reaction mixture was dissolved in 2.5 L of dichloromethane, precipitated in 6.5 L of methanol and dried. Yield: 327 g (73.3%) pale yellow powder.

Step 2: 100 g ($\sim$ 2.38 mmol) product of step 1 is dissolved in a three neck flask in 1.5 L toluene. The intensive yellow solution is purged with nitrogen and 3.07 mL (40 mmol) hexylamine is added by a syringe through a septum. After 48 h at slightly enhanced temperature, the reaction mixture was discolored.

Under intense nitrogen purging and heating up to 85°C, the remaining hexylamine was evaporated. After this 7.84 mL (75.8 mmol) bromoethanol und 19.2 g (139 mmol) annealed K_2CO_3 were added and stirred for 72 h at 85°C.

Figure 7. Comparison of the heat distortion temperature and the ultimate tensile strength of block copolymers DC2a and DC2b differing in the molar masses of the PS-macroinitiators. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Following, the reaction mixture was filtrated, precipitated in 4 L of methanol and the polystyrene was dried. Yield: 93.2 g (93.2%) white powder.

Ring Opening Polymerization of L,L-Lactide Initiated Via Polystyrene Macroinitiators. DC1: 3 g polystyrene macroinitiator **M1** and 10 mL dry toluene are mixed in a condensation vessel and heated up to 190°C under nitrogen purging. After a few millilitres toluene were distilled off, 27 g (187 mmol) L-lactide, and 5 min later 875 μL tin(II) 2-ethylhexanoate (1% in toluene) were added. After 2h the nitrogen flow is stopped and 150 mL chloroform are added to the hot melt. The mixture is cooled to room temperature and precipitated in 1.2 L of methanol. The copolymer is dried, extracted with methanol in a soxhlet and dried again. Yield: 27.4 g (91.3%) white fibers.

DC2a: 6 g polystyrene macroinitiator **M1** and 10 mL dry toluene are mixed in a condensation vessel and heated up to 190°C under nitrogen purging. After a few millilitres toluene were distilled of, 24 g (167 mmol) L-lactide and 5 min later 778 μL tin(II) 2-ethylhexanoate (1% in toluene) were added. After 2h the nitrogen flow is stopped and 150 mL chloroform are added to the hot melt. The mixture is cooled to room temperature and precipitated in 1.2 L of methanol. The copolymer is dried, extracted with methanol in a soxhlet and dried again. Yield: 26.2 g (87.3%) white fibers.

DC2b: analogous to **DC2a**, but with 6 g polystyrene macroinitiator **M2** instead of **M1**. Yield: 27.2 g (90.7%) white fibers.

DC3: analogous to **DC2a**, but with 9 g polystyrene macroinitiator **M1**, 21 g (146 mmol) lactide, 681 μL tin(II) 2-ethylhexanoate(1% in toluene). Yield: 25.6 g (85.3%) white fibers.

TC1: analogous to **DC2a**, but with 3 g polystyrene macroinitiator **M3**, 27 g (187 mmol) lactide, 1.75 mL tin(II) 2-ethylhexanoate (1% in toluene). Yield: 26.8 g (89.3%) white fibers.

TC3: analogous to **DC2a**, but with 9 g polystyrene macroinitiator **M3**, 21 g (146 mmol) lactide und 2.27 mL tin(II) 2-ethylhexanoate(1% in toluene). Yield: 27.4 g (91.3%) white fibers.

Analytics
The composition of the copolymers was determined by ^{1}H-NMR-spectroscopy using a Varian Unity 500-spectrometer ($CDCl_3$, 500 MHz).
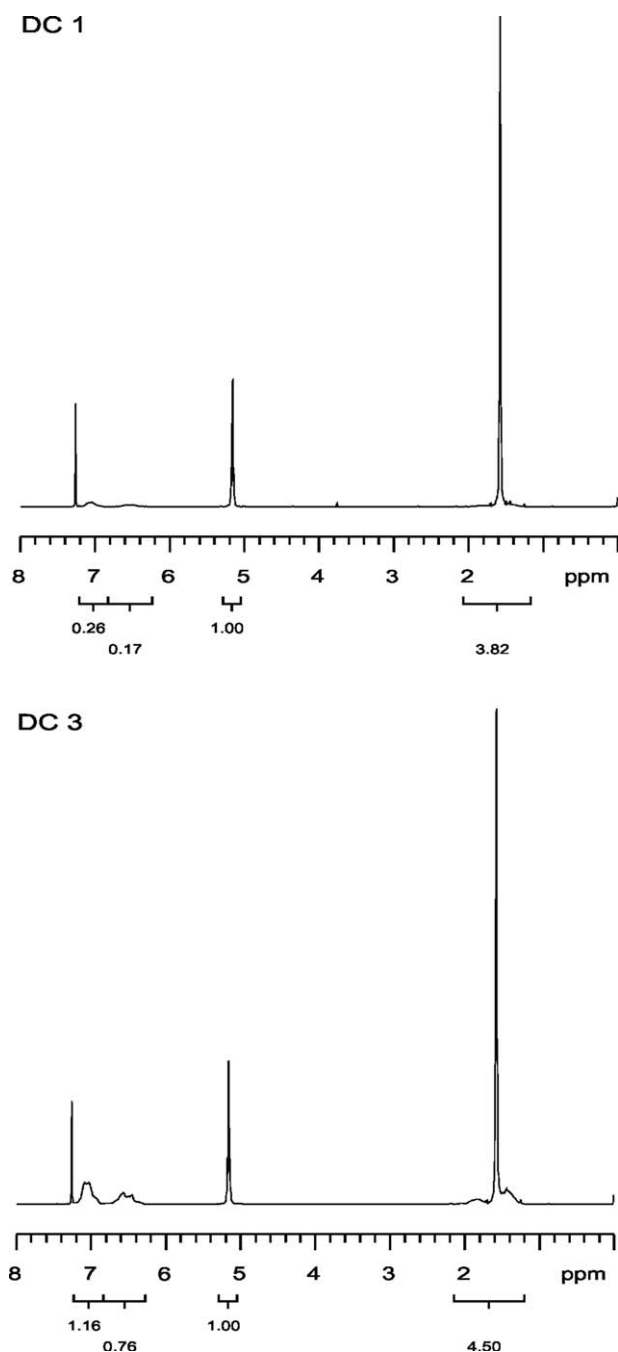
Figure 9. NMR-spectra of DC1 and DC3.

CONCLUSIONS

It could be shown that it is possible to increase the property profile of PLLA through formation of block copolymers with styrene. These block copolymers were synthesized by using hydroxyl functionalized polystyrenes as macroinitiator in the ROP of L-lactide.

The block copolymers possess higher molecular weights than reported for such polymers up to now and a high content of biobased PLLA. Even with PS contents as low as 10% the HDT as well as the mechanic properties of the block copolymers are improved compared with pure PLLA.

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As an example, Figure 9 shows the NMR-spectra of **DC1** and **DC3**.

The molecular weights of the macroinitiators and the block copolymers were determined by SEC (Waters, Shodex RI-Detector and eluent dichloromethane, standard calibration with PS standards).

The test specimen for mechanical and thermal testings were produced with a Haake-Minijet. HDT-B was analysed by TA Instruments-DMA 2980 and the mechanical properties by a tensile test (Zwick-materials testing machine 1445).

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