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Telechelic polylactones functionalized with trimethoxysilyl groups

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Abstract

Telechelic poly(ε-caprolactone)s or poly(D,L-lactide)s were prepared by $SnOct_2$-initiated polymerization of ε-caprolactone (εCL) or D,L-lactide (D,L-LA) coinitiated with 1,4-butane diol or tetra(ethylene glycol). These telechelic polyesters were in situ functionalized with 3-isocyanatopropyl trimethoxysilane (IPTMS) by $SnOct_2$-catalized addition of the OH-endgroups. Analogously, star-shaped polyesters were synthesized and functionalized using 1,1,1-trishydroxymethyl propane or pentaerythritol as coinitiators. All functionalized polymers were characterized by ^1H NMR and MALDI-TOF mass spectra. In crosslinking experiments with oligo(ethylene–glycol)s the trimethoxysilyl groups proved to be 10–30-fold more reactive than triethoxysilyl end-capped polyesters.

Keywords: ε-Caprolactone; D,L-Lactide; Tin(II)octanoate

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1. Introduction

In a parallel publication [1] we have reported on syntheses of monofunctional telechelic and star-shaped poly(ε-caprolactone)s functionalized with triethoxysilyl groups. These polylactones were prepared by $SnOct_2$-initiated ring-opening polymerization of εCL coinitiated with methylalcohol, diols, triols or tetraols (Scheme 1). After almost complete conversion, these OH-terminated polylactones were in situ functionalized by reaction with 3-isocyanatopropyltriethoxysilane (IPTMS). The isocyanate group proved to be reactive enough to allow for a selective reaction with the CH_2OH endgroups and side reactions with ethoxysilyl groups (Eq. (1)) were not observed. Whereas the relatively low reactivity of the triethoxysilyl groups is an advantage for clean syntheses of functionalized polylactones, it is a shortcoming for all applications requiring rapid reactions of the trialkoxysilyl groups with OH-groups on surfaces of various materials. In other words, for applications as adhesives, glues or coatings requiring short reaction times, the triethoxysilyl groups are not reactive enough. At this point it should be mentioned that telechelic poly(εCL)s and polylactides end-capped with two triethoxysilyl groups were reported by three other research groups [2–4]. These telechelic polymers were prepared by a ‘two-step procedure’ and used for synthesis of inorganic/organic hybride networks. To the best of our knowledge polyesters end-capped with trimethoxysilyl groups have not been described before.

Therefore, it was the purpose of the present work to attempt syntheses of the polylactones **1a**,**b**, **2a**,**b**, **3a**,**b** and **4a**,**b** functionalized with trimethoxy silyl groups by a ‘one-pot procedure’. Decisive for the success of these syntheses was the problem, how fast is the side reaction of OH-endgroups with trimethoxy silyl groups (Eq. (1)) relative to the desired addition onto isocyanate groups. $SnOct_2$ may, in principle, catalyze both reactions, but not necessarily at the same rate. However, for a ‘one pot procedure’ the presence of $SnOct_2$ was unavoidable, and thus, the catalytic role of $SnOct_2$ was an important part of the problem. In this connection it should be mentioned that the mechanism of ring-opening polymerization initiated by the combination of $SnOct_2$ with an alcohol was recently elucidated by Kricheldorf et al. [5] and Penczek et al. [6,7].

2. Experimental

2.1. Materials

ε-Caprolactone (εCL), Sn(II)2-ethylhexanoate ($SnOct_2$), benzylalcohol, 1,4-butane diol, tetra(ethylene glycol), TEG, 1,1,1-*tris*(hydromethyl)propane (THMP), and pentaerythritol and ethoxylated pentaerythritol (15 ethoxy groups) were purchased from Aldrich Co. (Milwaukee, WI, USA). ε-Caprolactone was distilled in vacuo over powdered CaH_2. The diols

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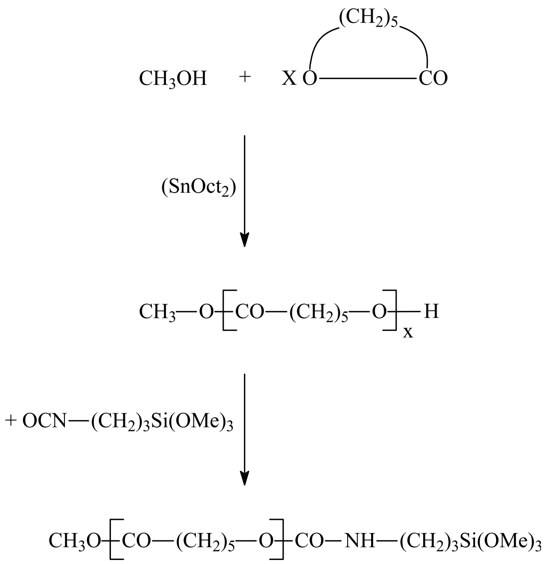

Scheme 1.

were azeotropically dried with toluene and distilled over a short-path apparatus in a vacuum of 10^{-2} mbar. The triol and the tetraols were dried in a desiccator over P_4O_{10}. The $SnOct_2$ was purified as described previously [5]. Racemic D,L-lactide was kindly supplied by Boehringer KG (Ingelheim, Germany). It was recrystallized from dry ethyl acetate with addition of ligroin and stored in a desiccator over P_4O_{10}. 3-Isocyanatopropyltriethoxysilane (IPTMS) was purchased from ABCR Chemicals (Karlsruhe, Germany) and used as received. Dichloromethane, chloroform and chlorobenzene were distilled over P_4O_{10}.

2.2. Polymerizations of εCL

εCL (40 mmol) and 1,4-butane diol (1 mmol) were weighed under dry nitrogen into a 50 mL Erlenmeyer flask having silanized glass walls. The closed reaction vessel was placed into an oil bath preheated to 120 °C. After homogenization by shaking, 0.16 mL of a 0.5 M $SnOct_2$ solution in dry chlorobenzene were injected and the heating was continued for 4 h. After cooling, the virgin product was dissolved in dry chloroform (20 mL) and IPTMS (2.06 mmol) was injected, and the solution was stirred at 50 °C for 16 h. The chloroform was then removed in vacuo, and the remaining crude product was characterized (No. 1, Table 1). In an analogous experiment 60 mmol of ε-CL was used (No. 2).

Table 1
$SnOct_2$-initiated polymerization of ε-caprolactone with in situ functionalization by means of IPTMS

Exp. no.	Coinitiator	εCL/coinitiator	Arm lengths (^{1}H NMR)	η_{inh}[a] (dL/g)	Temp. (°C)
1	1,4-Butane diol	40/1	19.7	0.19	120
2	1,4-Butane diol	60/1	30.0	0.31	120
3	Tetra(ethylene glycol)	40/1	19.6	0.21	80
4	Tetra(ethylene glycol)	60/1	20.5	0.32	80
5	1,1,1-*Tris*(hydroxy-methyl) propane	60/1	19.5	0.27	120
6	Pentaerythritol	80/1	19.3	0.36	120
7	EO-Pentaerythritol[b]	80/1	19.5	0.43	120

[a] Measured at 20 °C with $c=2$ g/L in CH_2Cl_2.
[b] Ethoxylated pentaerythritol (containing 15 ethoxy groups).

Table 2
$SnOct_2$-initiated polymerization of D,L-lactide (140 °C/0.5 h) with in situ functionalization by means of IPTMS

Exp. no	Coinitiator	DL−LA/coinitiator	Arm lengths (^{1}H NMR)	η_{inh}[a] (dL/g)
1	Benzyl alcohol	20/1	20.4	0.10
2	1,4-Butane diol	40/1	19.8	0.20
3	Tetra(ethylene glycol)	40/1	19.8	0.21
4	1,1,1-*Tris*(hydroxy-methyl)propane	60/1	20.4	0.18
5	Pentaerythritol	80/1	21.0	0.21

[a] Measured at 20 °C with $c=2$ g/L in CH_2Cl_2.

In a parallel experiment, small samples were taken from the chloroform solution every hour, and the conversion was checked by IR and ^{1}H NMR spectroscopy. After 16 h, a conversion around 99% was achieved. All other experiments listed in Table 1 were performed analogously. However, with THMP or pentaerythritol as coinitiators the initial homogenization by shaking was performed at 140 °C before the temperature was lowered to 120 °C. When TEG was used as coinitiator, the polymerization temperature was lowered to 80 °C for 20 h (Nos 3 and 4, Table 1).

2.3. Polymerizations of D,L-lactide (No. 1, Table 2)

D,L-lactide (30 mmol) and benzylalcohol (1.5 mmol) were weighed under dry nitrogen into a 50 mL Erlenmeyer flask having silanized glass walls. After homogenization at 140 °C,

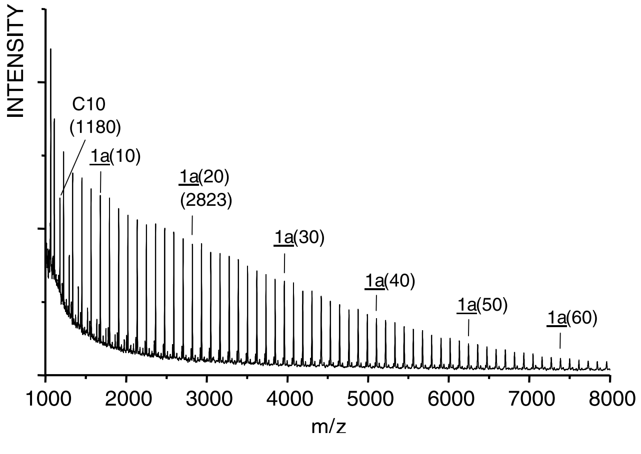

Fig. 1. MALDI-TOF mass spectrum of the 1,4-butane diol-initiated poly(εCL) functionalized with IPTMS (No. 1, Table 1). The numbers in brackets indicate the degrees of polymerization. C means cyclic oligolactones.

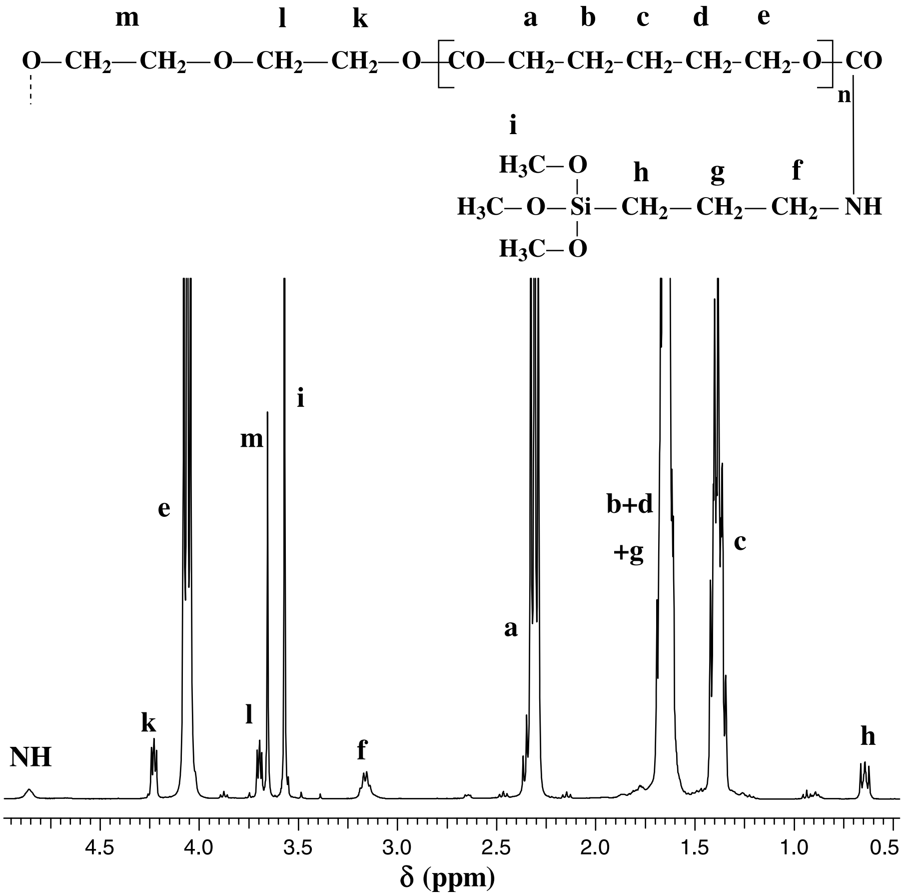

Fig. 2. Four hundred megahertz ^{1}H NMR spectrum of the TEG-initiated poly(εCL) functionalized with IPTMS (**2a**, No. 3, Table 1).

0.12 mL of a 0.5 M $SnOct_2$ in dry chlorobenzene were injected and the polymerization was conducted for 0.5 h at 140 °C, whereby a conversion around 97% was achieved (conversions around 99 or more % are for thermodynamic reasons not possible). After cooling, the poly(D,L-lactide) was dissolved in dry chloroform and functionalized with IPTMS (1.55 mmol) at 50 °C for 16 h. The crude reaction product was characterized.

All other experiments listed in Table 2 were conducted analogously.

2.4. Measurements

The inherent viscosities were measured in dry CH_2Cl_2 with an automated Ubbelohde viscometer thermostated at 20 °C. The glass walls of the capillary were silanized with a solution of dichlorodimethylsilane in diethyl ether and dried at 80 °C in vacuo before use. The 400 MHz ^{1}H NMR spectra were recorded on a Bruker ‘Avance 400’ FT spectrometer in 5 mm o.d. sample tubes. $CDCl_3$ containing TMS served as solvent and shift reference. The 100.24 MHz ^{13}C NMR spectra were recorded with the same spectrometer under the same conditions. The MALDI-TOF mass spectra were measured on a Bruker ‘Biflex III’ mass spectrometer equipped with a nitrogen laser ($\lambda = 337$ nm) All spectra were measured in the reflection mode with an acceleration voltage of 20 kV. The irradiation targets were prepared from chloroform solutions with dithranol as matrix and potassium trifluoroacetate as dopant.

3. Results and discussion

3.1. Poly(ε-caprolactone)s

In order to obtain telechelic poly(εCL) of structure **1a**, εCL was polymerized in bulk with 1,4-butane diol as coinitiator. Monomer/coinitiator ratios of 40/1 and 60/1 were used (Nos 1 and 2, Table 1). Reaction time and temperature allowing for almost complete conversions were known from previous studies [1,8]. The almost complete conversion and the chemical structure of the poly(εCL) was checked by ^{1}H NMR spectroscopy prior to the addition of IPTMS. The reaction with IPTMS in chloroform at 50 °C was monitored by IR spectroscopy and ^{1}H NMR spectroscopy. In the IR spectra the disappearance of the ‘isocyanate bands’ at 2885 and 2975 cm^{-1} was considered to indicate complete conversion. In the ^{1}H NMR spectra the triplet of the $-CH_2-NCO$ group at 3.3 ppm vanished, whereas the multiplet of the $-CH_2NH-CO$ group appeared at 3.1 ppm. In this way, it was found that a reaction time of 16 h suffices for the complete addition of IPTMS. The structure of the polylactone **1a** was confirmed by MALDI-TOF mass spectrometry. However, the mass spectrum (m.s.) presented in Fig. 1 also evidenced that the telechelic polylactone contained a small fraction of cyclic

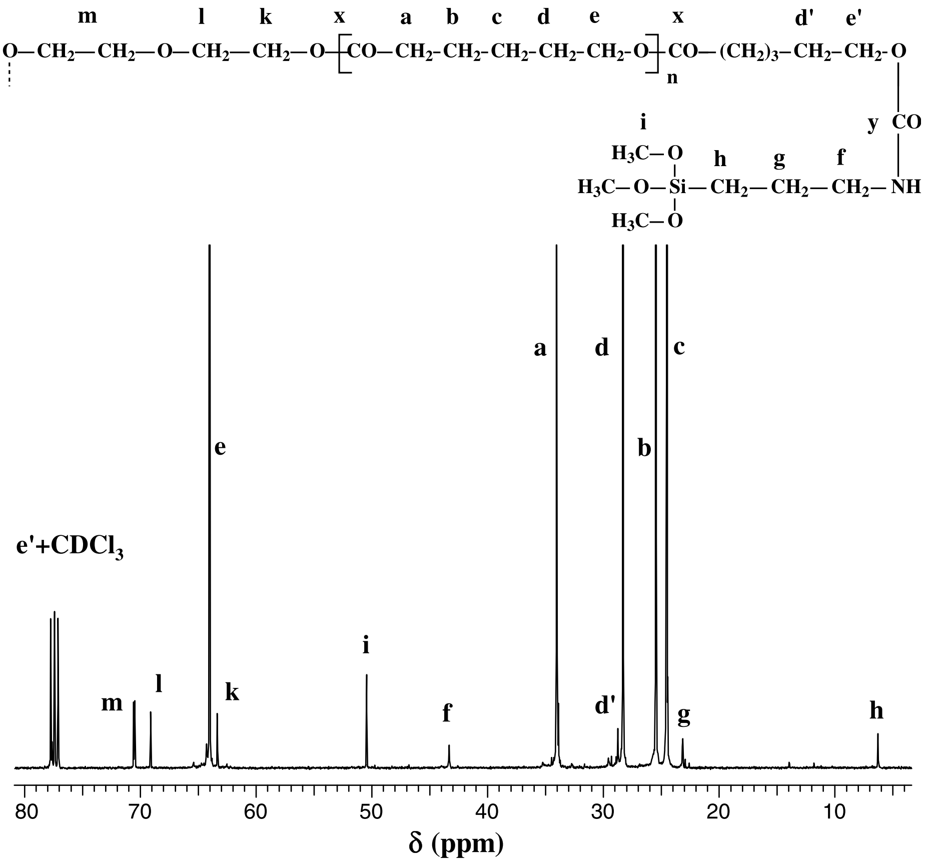

Fig. 3. 100.4 MHz ^{13}C NMR spectrum of the TEG-initiated poly(εCL) functionalized with IPTMS (**2a**, No. 3, Table 1). The CO signals at 156.7 and 173.3 ppm are not displayed.

oligolactones (symbol C). This byproduct resulted from 'back-biting degradation' during the synthesis of the parent OH-terminated poly(εCL). This is a typical consequence of almost all tin-initiated polymerizations of εCL around or above 100 °C. In agreement with the existence of efficient equilibration reactions a broad frequency distribution was found (Fig. 1) which resembles that of polycondensates resulting from a step-growth polymerization.

Two analogous experiments were conducted with TEG as initiator (Nos 3 and 4, Table 1). This monodisperse oligo(ethylene glycol) was used as model compound of higher, polydisperse oligo- and poly(ethylene glycol)s. The monodispersity of TEG has the advantage that the resulting polylactones may be characterized by MALDI-TOF mass spectrometry. Prior to the characterization with mass spectrometry, the crude product was characterized with ^{1}H and ^{13}C NMR spectroscopy. The good agreement between the expected structure (**2a**) and NMR spectra is demonstrated by Figs. 2 and 3. The m.s. presented in Fig. 4 confirmed structure **2a**. Furthermore, two interesting differences were found when compared to the butane diol-initiated polylactones (**1a**). First, the content of cyclic oligolactones was considerably lower, obviously a consequence of the lower polymerization temperature. Second, the frequency distribution was different, it was narrower than in the case of **1a**. This observation may again be explained by a lower extent of equilibration reactions (e.g. back-biting degradation) which has the tendency to broaden an initially narrow molecular weight distribution. Regardless which diol was used as coinitiator, no gel particles were observed, what indicates that the 'one-pot procedure' used in this work was successful, and did not involve significant side reactions of the trimethoxysilyl groups.

When the tri- or tetrafunctional alcohols were used as coinitiators (Nos 5 and 6, Table 1), heating with εCL to 140 °C for a few minutes was required to obtain a homogeneous phase. The ring-opening polymerization initiated by addition of

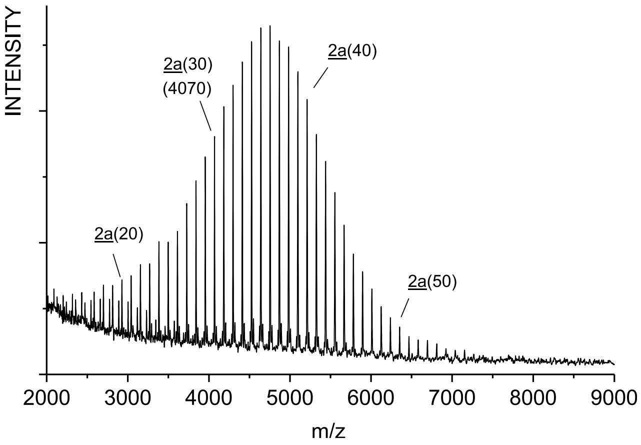

Fig. 4. MALDI-TOF mass spectrum of the TEG-initiated poly(εCL) functionalized with IPTMS (**2a**, No. 3, Table 1). The numbers in brackets indicate the degrees of polymerization.

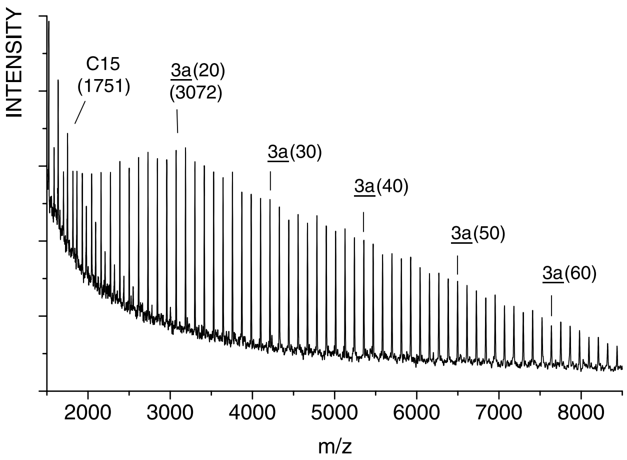

Fig. 5. MALDI-TOF mass spectrum of the THMP-initiated poly(εCL) functionalized with IPTMS (**3a**, No. 5, Table 1). The numbers in brackets indicate the degrees of polymerization.

$SnOct_2$ and the functionalization with IPTMS were performed quite analogously to the above described syntheses of **1a** and **2a**. Again, perfectly soluble reaction products of structure **3a**, **4a** and **5a** were obtained. Their structure was confirmed by ^1H and ^{13}C NMR spectroscopy and by MALDI-TOF mass spectrometry. The m.s. of **4a** is displayed in Fig. 5 as characteristic example. Finally, it should be mentioned that the inherent viscosities reflect the monomer/coinitiator ratios. SEC measurements were not conducted to avoid misinterpretations resulting from side reactions (e.g. hydrolysis) of the reactive trimethoxysilyl groups.

3.2. Poly(D,L-lactide)s

The successful syntheses of trimethoxysilyl endcapped polylactones prompted us to attempt analogous syntheses of functionalized poly(D,L-lactide)s. The high melting point of D,L-lactide (around 125 °C) required that the homogenization with the coinitiator was performed at 140 °C. Due to this higher temperature and due to the higher reactivity of D,L-lactide (relative to εCL), a polymerization time of 0.5 h sufficed to achieve $\geq 97\%$ conversion. The functionalization with IPTMS was then conducted in chloroform at 50 °C with a reaction time of 16 h. After removal of the chloroform, the crude reaction products were characterized by viscosity measurements, by ^1H and ^{13}C NMR spectroscopy and by MALDI-TOF mass spectrometry. In all cases, the spectra agreed with the expected structures **1b–5b** and **6**. The ^1H NMR spectrum of the butane diol-initiated poly(D,L-lactide), No. 2, Table 2, is presented as a typical example in Fig. 6. However, a few side reactions were detectable. For instance, the ^1H NMR spectra revealed a singlet signal at 3.75 ppm (signal x in Fig. 6) which, by comparison with a model compound, may be attributed to a methyl urethane group resulting from the reaction of liberated methanol (e.g. by hydrolyses of trimethoxysilyl groups) with the isocyanate group of IPTMS. The MALDI-TOF m.s. evidenced the presence of a small fraction (presumably ≤ 3 wt%) of cyclic oligolactides. Since the cyclic oligolactones and oligolactides are non-toxic and biodegradable, and since they do not interfere with reactions of the trimethoxysilyl groups, their presence should not affect any potential application of the trimethoxysilyl functionalized polyesters prepared in this work.

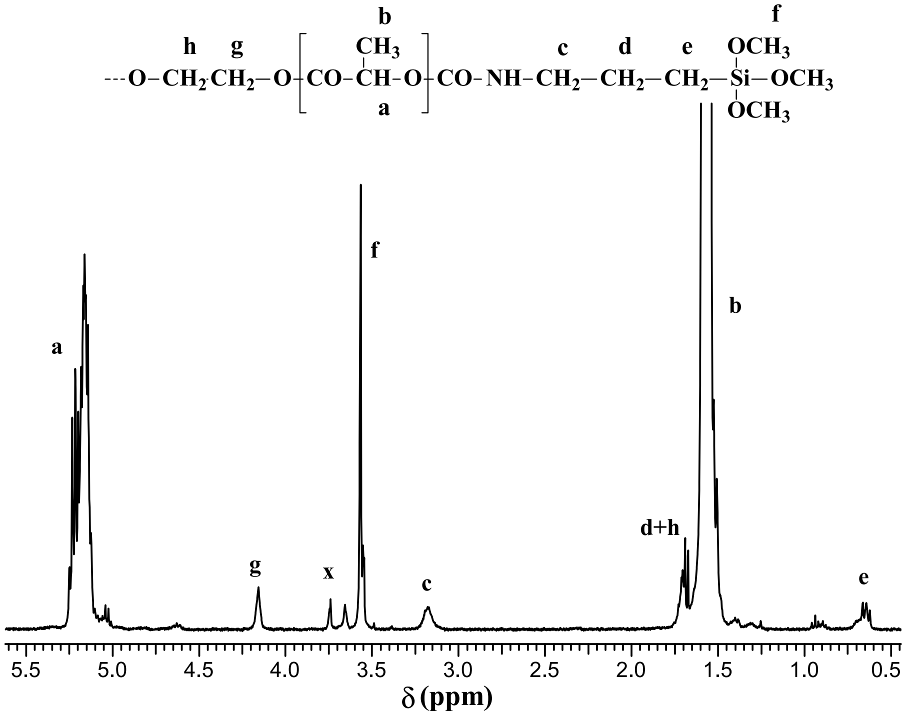

Fig. 6. Four hundred megahertz ^1H NMR spectrum of the butane diol-initiated poly(D,L-lactide) functionalized with IPTMS (**1b**, No. 2, Table 2).

Table 3
Crosslinking experiments with poly(εCL) **4a** (arm length ∼20) and a double molar amount of PEG-600 in bulk at 60 °C

Exp. no.	Catalyst[a]	Reaction time needed for gelation	
		4a+PEG-600	**7**+PEG-600
1	Without catalyst	2.0	72
2	$Bu_2Sn\ (OAc)_2$	1.5	16
3	*p*-Toluene sulfonic a.	0.5	10
4	Dabco[b]	10.0	96

Comparison with the triethoxysilyl functionalized analog **7**.

[a] Molar ratio **4a** (or **7**)/coinitiator=500/1.

[b] Diazabicyclo octane

3.3. Crosslinking experiments

A few model reactions were conducted with the purpose to illustrate the assumed higher reactivity of trimethoxy versus triethoxysilyl groups in the formation of gels or in adhesion. These model reactions were performed in such a way that poly(ethylene glycol)-600 and equimolar amounts of the poly(εCL) **4a** or an analogous triethoxysilyl-terminated poly(εCL) **7** (synthesized previously) [1] were heated at 60 °C in bulk. The time required until gelation became detectable was determined and listed in Table 3. Three kinds of catalysts were added, a tin compound typically used as catalyst for the formation of urethanes or for transesterification, 4-toluene sulfonic acid and diaminobicyclooctane as an example of a basic catalyst. The results clearly demonstrate that the trimethoxysilyl groups are by a factor 10–30 more reactive than the triethoxysilyl groups. Furthermore, the toluene sulfonic acid proved to be a good catalyst, whereas DABCO efficiently hindered the reaction. In summary, the trimethoxysilyl groups are the far more attractive reaction partners when rapid crosslinking is required.

4. Conclusion

The results reported above prove that the ‘one-pot procedure’ elaborated in this work allows for successful syntheses of trimethoxysilyl functionalized polylactones and poly(D,L-lactide)s. Polyesters containing one, two, three or four trimethoxysilyl groups were prepared without significant side reactions of the methoxysilyl groups. As reported for triethoxysilyl endcapped polylactones [1], the number of alkoxysilyl groups in one molecule has an enormous influence on its reactivity toward reactants bearing OH-groups. Therefore, the versatility of the approach described above allows for optimization of the properties for a variety of potential applications such as coatings, adhesives and syntheses of hybrid networks.

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