Synthesis and structures of cooligo(lactone) macromonomers

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SUMMARY: Cooligo(lactone) macromonomers were prepared by cooligomerisation of (S,S)-3,6-dimethyl-1,4-dioxane-2,5-dione (L-lactide), 1-oxacyclohexane-2-one (δ-valerolactone) or 1-oxacycloheptane-2-one (ε-caprolactone), initiated by 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]-propane (BisGMA). Two different reaction ways were used for the synthesis: parallel reaction and step reaction of lactones and L-lactide. The macromonomers were characterised by differential scanning calorimetry (DSC), size exclusion chromatography (SEC), ^{1}H- and ^{13}C-NMR spectroscopy and MALDI-TOF mass spectrometry. Cooligo(lactone) macromonomers prepared by parallel and by step reaction show different molecular structures resulting in different properties. Their glass transition temperatures depend on the molar ratio of lactide and lactone as well as on the degree of oligomerisation. Macromonomers with high amounts of L-lactide units are partially crystalline.

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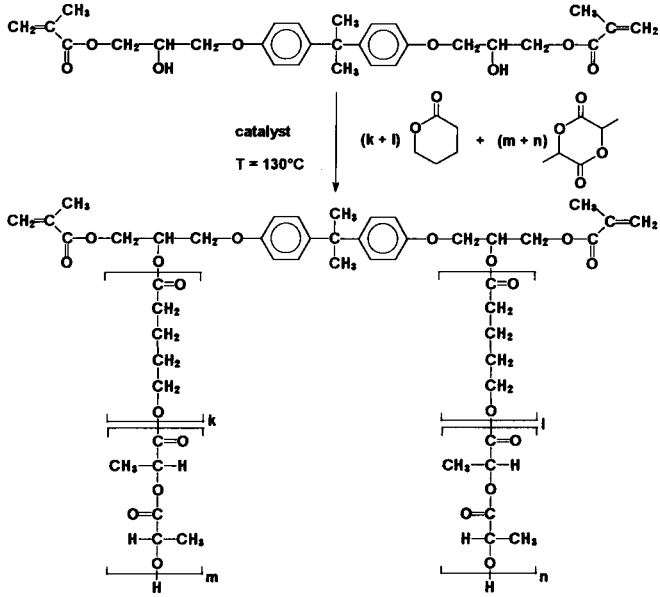
Introduction

Poly(lactide) and its copolyesters are of increasing interest as biodegradable materials for pharmaceutical and medical applications. For these purposes, the polymers should be completely degradable. However, a complete degradation of very high molecular poly(L-lactide) is not achieved, but disintegration into microcrystalls [1,2]. The latter cause inflammation of the living tissue [3]. Therefore, a material resulting in a coherent framework, e. g. for the ingrowth of bone cells after partial degradation, should be of interest for some applications.

One method to prepare such partially biodegradable polymers is the free radical copolymerisation of oligo(lactide) macromonomers and a diluting monomer, like tri(ethyleneglycol) dimethacrylate or 2-hydroxyethyl methacrylate. The result of this copolymerisation procedure is a crosslinked polymer backbone grafted with degradable oligo(lactide) branches [4]. Various methods to prepare oligo(lactone) macromonomers are known [4-13]. The polymerisation of L-lactide and several lactones, catalysed by $Sn(oct)_2$, proceeds according to an insertion mechanism with living character.



Reaction scheme of the step cooligomerisation of δ-valerolactone (VL) and L-lactide (LLA) initiated by BisGMA.

The oligomerisation of lactide initiated by 2,2-bis[4-(2-hydroxy-3-methacryloyloxy propoxy) phenyl] propane (BisGMA) shows also living character as proved recently [13]. Taking advantage of these conditions, block cooligomers can be obtained. The aim of this work has been the synthesis of cooligo(lactone) macromonomers initiated by BisGMA. The two hydroxyl groups of BisGMA are able to initiate the ring-opening polymerisation of various lactones. The detailed reaction procedure with L-lactide and D,L-lactide as well as for cooligomerisation of L-lactide with ε-caprolactone and glycolide, respectively, has been described recently [4,13]. The cooligomerisations were carried out as parallel reaction of both components. Here, the course of parallel and step reactions as well as the structures of cooligo(lactone) macromonomers obtained will be compared.

Experimental

Materials: BisGMA was prepared as described in ref. [14]. L-lactide (LLA) (Boehringer Ingelheim) was purified by recrystallization from ethyl acetate and dried in vacuo. δ-valerolactone (VL) and ε-caprolactone (CL) were distilled under reduced pressure. Stannous(II)-octoate (Sigma Chemical), 2,6-di-(1,1-dimethylethyl)-4-methylphenol (Ionol, BHT) (Merck) and deuterated chloroform ($CDCl_3$) were used as received. Tetrahydrofuran (THF) was dried over KOH and rectified. Poly(propyleneglycol) standards (molecular weight range from 76 Da to 5430 Da) were obtained from Polymer Standards Service, Germany, and polystyrene standards (molecular weight range from 580 Da to 22000 Da) were obtained from Showa Denko, Japan.

Synthesis of oligo(lactone) macromonomers

Parallel reaction: Both comonomers (e. g. LLA and VL), the initiator BisGMA, the catalyst $Sn(oct)_2$ and the inhibitor Ionol (0.1 wt.% rel. to BisGMA) were mixed in the reaction vessel under stirring and heating at 130 C. The typical molar ratio of catalyst to initiator was 0.02. The reaction time was varied from six to eight hours dependent on the concentrations of lactone and lactide. The oligomerisations were stopped, when no further increase in the oligomerisation degree was detected by SEC measurements.

Step reaction: First the less reactive comonomer, the lactone, was oligomerised initiated by BisGMA in the presence of $Sn(oct)_2$ and the inhibitor Ionol at 130 C. After attaining the limiting conversion of the lactone (about four hours), LLA was added.

Analysis

SEC measurements were carried out on a Knauer device with three Hibar RT columns (PS 1, PS 4 and PS 20), a differential refractometer as detector and THF as solvent at a flow rate of 1 ml/min. The three eluation peaks of the macromonomer, of LLA and the lactone could be separated by means of the combination of SEC columns. The conversions of LLA and the lactones were determined from the peak areas after calibration for their concentrations. The molecular weights of the macromonomers were computed by calibration curves based on poly(propyleneglycol) (PPG) and polystyrene (PS) standards, respectively.

NMR spectra were measured on a Varian Gemini 2000 spectrometer at frequencies of 75 MHz (^{13}C-NMR) and 300 MHz (^{1}H-NMR). About 10 wt. % of the macromonomers were dissolved in $CDCl_3$ containing tetramethylsilane (TMS) for shift reference. Quantitative ^{13}C-NMR-spectra were recorded by the method of the inverse gated decoupling to obtain a proton noise decoupled spectrum and also to avoid the Nuclear Overhauser Effect. The carbonyl carbon atoms showed the highest spin-lattice relaxation times T_1 of about 8 seconds. Therefore, a delay time of 40 seconds (five times as long as the highest T_1) was chosen. Up to 4000 transients were accumulated.

MALDI-TOF mass spectra were recorded on a Shimadzu MALDI-III-spectrometer in the presence of 1.8.9-trihydroxyanthracene serving as matrix and sodium trifluoroacetate. A poly(ethyleneglycol) standard of 1450 g/mol was used for calibration.

The thermal properties of the macromonomers were determined by DSC using a Perkin Elmer DSC 7 device. The heating rate was 10 K/min.

Results and discussion

Synthesis of macromonomers

A step reaction procedure can be used to synthesise cooligo(lactone) macromonomers with blocky sequences. Copolymerisations of LLA and VL or CL with $Sn(oct)_2$ as catalyst are characterised by a larger reactivity of LLA [15]. That is why the less reactive lactones were oligomerised first as shown in the reaction scheme. However, even after very long reaction times, a complete conversion of the lactones could not be accomplished. As shown in Tab. 1, the limiting conversion of VL is about 85 % and that of CL is about 90 % under the conditions mentioned. LLA was added to the addition product of BisGMA and lactone, when no further increase in the number-average molecular weight of the oligo(lactone) macromonomers could be observed. The conversion of LLA was almost complete. Parallel reaction of LLA with VL or CL resulted in nearly complete conversion of LLA, too. However, the limiting conversion of the lactones was lower than that in the step reaction (see Table 1).

Table 1: Limiting conversions of lactones determined by SEC

Macromonomer composition	Mole ratio	React. type[a]	Limiting conversion of	Limiting conversion [%]	Limiting conversion [%] after add. of LLA
BisGMA:VL:LLA	1.2:8	pll	VL	82	-
BisGMA:VL:LLA	1:2:8	step	VL	84	93
BisGMA:VL	1:8	-	VL	88	-
BisGMA:CL:LLA	1:2:8	step	CL	93	93
BisGMA:CL	1:10	-	CL	88	-

[a] Reaction type: step or parallel reaction

Determination of the molecular weights

The molecular weights of the macromonomers were controlled by means of SEC both calibrated with poly(propyleneglycol) and poly(styrene) standards. Additionally, M_n of the macromonomers were computed from the molar ratios of BisGMA and LLA as well as lactone and from their conversion data measured by SEC according to Equation 1.

$$M_n = M_{BisGMA} + M_{LAC} \cdot U_{LAC} \cdot \frac{n^0_{LAC}}{n^0_{BisGMA}} + M_{LLA} \cdot U_{LLA} \cdot \frac{n^0_{LLA}}{n^0_{BisGMA}} \qquad (1)$$

M_{LAC} = molecular weight of lactone

M_{LLA} = molecular weight of L-lactide

M_{BisGMA} = molecular weight of BisGMA

U_{LAC} = conversion of lactone

U_{LLA} = conversion of L-lactide

n^0_{LAC} = moles of lactone at the start of the oligomerisation

n^0_{LLA} = moles of L-lactide at the start of the oligomerisation

n^0_{BisGMA} = moles of BisGMA at the start of the oligomerisation

End-group analysis of the macromonomers by NMR spectroscopy offers another way to determine their M_n. The signals of the ^{1}H-NMR spectra instead of the signals of the quantitative ^{13}C-NMR spectra were used for the determination of M_n because of the better signal-to-noise ratio. The signals of the aromatic protons of BisGMA at chemical shifts of 6.8

and 7.15 ppm, the signals of the CO-C<u>H</u>$_2$ α-methylene protons of the lactones at δ= 2.3 ppm and the signal of the methine proton of (oligo)lactide at δ= 5.15 ppm were used for the determination of M_n. Two problems have to be mentioned in this context. Firstly, the signal of the methine proton of LLA (δ= 5.1 ppm) is covered by the signal of the methine proton of oligo(lactide). However, the conversion of LLA is usually higher than 98 %, and the error of the calculation will be negligible, if the amount of non-converted LLA is neglected. Secondly, the CO-C<u>H</u>-OH methine proton signal of the oligo(lactide) end-group (δ= 4.35 ppm) can not clearly be separated from methylene proton signals of BisGMA. Nevertheless, the number of lactide end-groups is necessary for the calculation of M_n. Thus, the intensity of the end-group signal was recomputed from the quantitative ^{13}C-NMR spectrum (shifts see Table 4). The molecular weights determined by the four different methods mentioned are displayed in Tab. 2.

Table 2: Comparison of different methods for determining the number-average molecular weight [g/mol] of cooligo(lactone) macromonomers

Macromonomer composition	Mole ratio	Rct. type	SEC-data PS standards	SEC-data PPG standards	^{1}H-NMR data	Calc. from conversion
BisGMA:VL:LLA	1:2:6	pll	1900	1370	1560	1530
BisGMA:VL:LLA	1:2:6	step	1980	1420	1540	1530
BisGMA:VL:LLA	1:2:8	pll	2290	1630	1940	1810
BisGMA:VL:LLA	1:4:6	pll	2130	1550	1700	1580
BisGMA:CL:LLA	1:2:8	pll	2250	1540	1840	1800
BisGMA:LLA	1:8	-	2060	1430	1690	1630
BisGMA:VL	1:8	-	1640	1150	1330	1220
BisGMA:CL	1:10	-	1830	1310	1500	1520

The molecular weights according to calibration with poly(propyleneglycol) are lower than the calculated ones. However, they correspond better to the ^{1}H-NMR data and to the conversion data than the SEC results with poly(styrene) calibration [16]. The calculation of the number-average molecular weight from ^{1}H-NMR and conversion data is based on the presumption, that no other molecules besides BisGMA act as an initiator and that chain degradation does not take place during the oligomerisation. If other molecules, especially moisture and impurities from the BisGMA synthesis, are able to initiate the ring-opening oligomerisation of lactide or lactone, the calculated M_n will be too large. The real molecular weights may have the magnitude of the SEC data from calibration with poly(propyleneglycol). The molecular weights calculated from calibration with poly(styrene) are too high in any case.

Table 3: Polydispersities of cooligo(lactone) macromonomers

Macromonomer composition	Mole ratio	Rct. type	M_w/M_n (SEC-data)
BisGMA:VL:LLA	1:2:6	pll	1,11
BisGMA:VL:LLA	1:2:6	step	1,17
BisGMA:VL:LLA	1:2:8	pll	1,13
BisGMA:VL:LLA	1:2:8	step	1,27
BisGMA:VL:LLA	1:4:6	pll	1,21
BisGMA:CL:LLA	1:2:8	pll	1,13
BisGMA:LLA	1:8	-	1,13
BisGMA:LLA	1:40	-	1,07
BisGMA:CL	1:10	-	1,41
BisGMA:VL	1:8	-	1,37
BisGMA:VL	1:40	-	1,28

As apparent in Table 3, the ratios M_w/M_n of the macromonomers, except lactone homooligomers, are lower than 1.3. The rather narrow molecular weight distributions are a sign of the living character of the oligomerisation. Most of the macromonomers obtained by parallel reaction have polydispersities even smaller than 1.2. The polydispersities of the products prepared by step reaction are usually larger. During the oligomerisation of lactones initiated with BisGMA the rate of propagation is higher than the rate of initiation. The addition of the lactone monomers at the primary hydroxyl groups of the growing chains is preferred, because the secondary hydroxyl groups of BisGMA are less reactive than the primary hydroxyl groups. These differences in reactivity yield an increase in the ratio M_w/M_n until every secondary hydroxyl group has started a growing chain or the limiting conversion of the lactone has been attained. After addition of LLA, there is a further, but only small increase in polydispersity. During the parallel reaction, the secondary hydroxyl groups of BisGMA rapidly react with LLA to start a growing oligomer chain. The difference in activity between the secondary hydroxyl group of BisGMA and the secondary hydroxyl group of a growing chain of oligo(L-lactide) seems to be insignificant. Considering these aspects, the products of the parallel reaction and the oligo(L-lactide) macromonomers may have smaller polydispersities than the products of the step reaction procedure and the oligo(lactone) macromonomers.

Structure analysis

The structure analysis of the macromonomers was performed by ^{13}C-NMR-spectroscopy. The chemical shifts of the ^{13}C-NMR signals were assigned by means of model compounds like homooligomers containing different initiators and by means of spectra recorded by the method of distortionsless enhancement by polarisation transfer (DEPT). Some chemical shifts were available from the literature [17,18]. The carbon signals displayed in Table 4 were used for determining the sequence distribution of the cooligo(ester) chains.

Table 4: Chemical shifts δ [ppm] of ^{13}C resonances of oligo(VL-CO-LLA) macromonomers

Carbon atom (origin)	Sequence	δ [ppm]
C=O (VL)	LA-VL	172.9
C=O (VL)	VL-VL	173.5
C=O (LA)	LA-LA-LA	169.9
C=O (LA)	VL-LA-LA + LA-LA-VL	170.5
C=O (LA)	VL-LA-VL	171.1
C=O (LA)	LA (end-group)	175.5
CH_2-O (VL)	VL-VL	64.2
CH_2-O (VL)	VL-LA	65.2
CH_2-OH (VL)	VL (end-group)	62.4
CH-OH (LA)	LA (end-group)	66.9
CH_2-O-VL (BisGMA)	VL (starting group)	63.1
CH_2-O-LA (BisGMA)	LA (starting group)	63.7
CH-O-VL (BisGMA)	VL (starting group)	70.4
CH-O-LA (BisGMA)	LA (starting group)	71.2

LA is the abbreviation for lactic acid.

Only the centres of the signals are assigned.

The end-groups of the oligomer have to be considered for the calculation of the sequence length. This is necessary, because the negligence of the end-groups results in incorrectly high block lengths for oligomers with low molecular weights. The average block length of VL and LLA units were calculated according to the following assumptions.

The average block length l_A of monomer units A in a high-molecular-weight copolymer containing comonomers A and B can be calculated from the diad distribution according to Eq. 2.

$$l_A = \frac{[AA]}{[AB]} + 1 \qquad (2)$$

l_A = average block length of A units

$[AA],[AB]$ = concentration of the corresponding diads

However, in the case of oligomers, the end-groups have to be considered because each end-group interrupts the sequence of the repeat units. If the ends of the oligomer chain are linked together conceptually, and if the polymer chain is regarded as a cyclic and endless chain, as usually done in the sequence analysis of polymers [19,20], the computed block lengths will be too high. Taking into account the end-groups as sequence terminating groups results in more realistic sequence numbers and significantly lower average block lengths.

The sequence distribution was determined for lactone and lactic acid units to simplify the calculating method. The block length of lactic acid units was transferred to lactide units. In the case of oligo(VL-co-LLA) macromonomers, AB diads can be distinguished from BA diads because the chain direction can be established. Lactone or lactic acid units connected to BisGMA are defined as starting groups. Lactone and lactic acid units at the oligomer chain end containing a hydroxyl group are considered as end-groups. These groups can be detected in the ^{13}C-NMR spectra (see Table 4). Starting groups and end-groups have the same effect on the sequence distribution, therefore, the distinction between both groups is not really necessary for the calculation. In the spectra of macromonomers prepared by step reaction a small signal at δ= 64.4 ppm appears, which could be identified as a transesterification product of lactone units at the end of the propagating chain, and methacrylic acid derived from BisGMA. These lactone units directly connected to methacrylic acid are also regarded as end-groups. A transesterification product of lactic acid and methacrylic acid could not be observed.

$$l_A = \frac{2 \cdot [AA]}{[AB]+[BA]+[A_{start}]+[A_{end}]} + 1 \qquad (3)$$

Eq. 3 was used for the determination of the average block lengths. The concentrations of the end-groups, the starting groups and the [VL-VL], [VL-LA], [LA-VL] diads can be taken from the intensities of the corresponding signals. The amount of the [LA-LA] diads - exactly it is one lactide unit - can be calculated from the intensities of the different signals of the carbonyl carbon atoms of lactide. However, the quantities of LA units and VL units directly connected

to BisGMA have to be taken into account because their carbonyl signals are covered by the carbonyl signals of LLA and VL, respectively.

Table 5: Average block length and end-groups of oligo(VL-co-LLA) macromonomers

Macromonomer composition	Mole ratio	Rct. type	Aver. block length of LLA units	Aver. block length of VL units	End-groups LLA units [%]	End-groups VL units [%]
BisGMA:VL:LLA	1:2:6	pll	2.5	1.7	91	9
BisGMA:VL:LLA	1:2:6	step	3.1	2.4	100	0
BisGMA:VL:LLA	1:2:8	pll	3.0	1.5	90	10
BisGMA:VL:LLA	1:2:8	step	4.6	2.2	100	0

Table 5 shows the results of the sequence analysis. The differences between the chemical structures of products prepared by step and by parallel reaction are visible. As expected, the block lengths of LLA units or exactly lactic acid units will increase, if the step reaction procedure is applied. No hydroxyl end-groups of VL units were found in the step reaction products. This fact could be verified by regarding the ^{1}H NMR spectra. The $C\underline{H}_2$-OH signal of the lactone end-group (δ= 3.6 ppm) did not appear.

The products of the parallel reaction contain only small quantities of hydroxyl end-groups of VL, although it is less reactive than LLA and should be fixed to the propagating chain last. It is the reason for the low content of hydroxyl end-groups of lactone units, that these lactone units are an active site for transesterification reactions. These transesterification reactions cause the changes of sequence lengths and generate new sequences [21]. In fact the VL-LA-VL triad sequence (LA means lactic acid) could be detected in the spectra of oligomers prepared by parallel reaction. This sequence can be formed by transesterification reactions only. The spectra of the macromonomers prepared by step reaction do not contain any signal of this triad.

The MALDI-TOF mass spectrum of an oligo(L-lactide) macromonomer indicates transesterification being an important side reaction of the oligomerisation of lactide (Fig. 1). The distances between two molar mass peaks are 72 Da, which correspond to the half of the molecular weight of LLA (M = 144.1 g/mol). This peak distance can only result from transesterification reactions occurring during the oligomerisation. Chain degradation can not cause this behaviour, because low molecular weight products of the degradation are not detected in the SEC chromatogram.

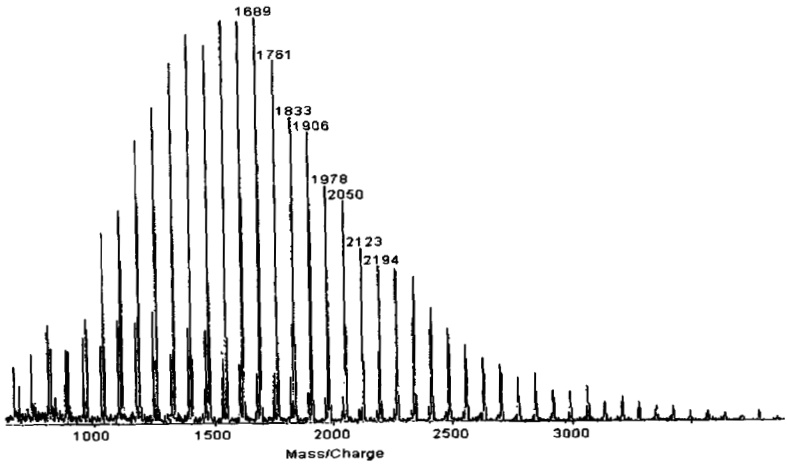


Figure 1: MALDI-TOF mass spectrum of an oligo(L-lactide) macromonomer with the molar composition BisGMA:LLA = 1:8

Theoretical molar mass: 1666 Da - detected as sodium-adduct at 1689 Da

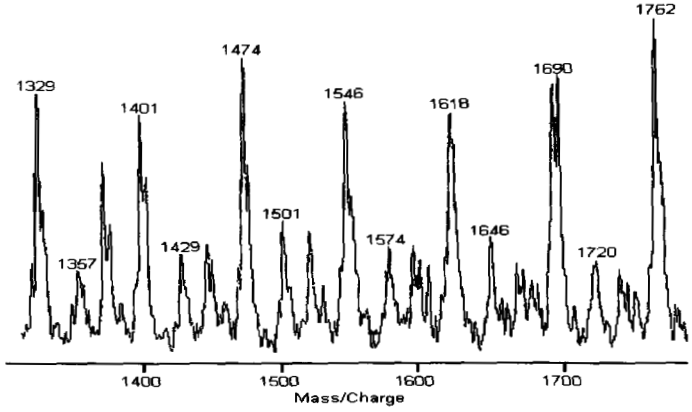


Figure 2: Part of a MALDI-TOF mass spectrum of a cooligo(lactone) macromonomer with the molar composition BisGMA:VL:LLA = 1:2:8

Only the signals of two different distributions are indicated.

Oligo(LLA) macromonomer:

512,6 Da (BisGMA) + 23 Da (Na) + x·(144,1/2) Da (LLA) where $11 \leq x \leq 17$

Oligo(VL-co-LLA) macromonomer containing one VL unit:

512,6 Da (BisGMA) + 23 Da (Na) + 100,1 Da (VL) + x·(144,1/2) Da (LLA)

where $10 \leq x \leq 15$; x is the half of the number of the lactide units.

MALDI-TOF mass spectra of cooligomers are complicated and more difficult to interpret (Fig. 2). Again peak distances of 72 Da can be observed, which implies transesterification reactions. The reaction product consists of a mixture of cooligo(lactone) macromonomers and of oligo(L-lactide) macromonomers. Molar mass peaks of both products are detected, whereas signals of oligo(valerolactone) macromonomers do not appear. This is another sign of the activity of VL units for transesterification reactions.

Thermal properties

The thermal properties of the macromonomers were investigated by DSC at a heating rate of 10 K/min. The glass transition temperatures (T_g) of the macromonomers are dependent on the amount of LLA and lactone as well as on the degree of oligomerisation.

Table 6: Thermal properties of macromonomers determined by DSC

Macromonomer composition	Mole ratio	Rct. type	T_g[a] [C]	T_m[b] [C]	ΔH_m[c] [J/g]
BisGMA:VL:LLA	1:4:6	pll	- 10	-	-
BisGMA:VL:LLA	1:4:6	step	- 6	-	-
BisGMA:VL:LLA	1:4:10	step	4	-	-
BisGMA:VL:LLA	1:2:6	pll	5	-	-
BisGMA:VL:LLA	1:2:6	step	0	-	-
BisGMA:VL:LLA	1:2:10	pll	14	-	-
BisGMA:VL:LLA	1:2:10	step	11	-	-
BisGMA:CL:LLA	1:2:6	step	5	-	-
BisGMA:CL:LLA	1:2:10	step	12	-	-
BisGMA:LLA	1:10	-	28	-	-
BisGMA:LLA	1:15	-	31	-	-
BisGMA:LLA[d]	1:15	-	29	108	20,7
BisGMA:LLA	1:20	-	39	-	-
BisGMA:LLA[d]	1:20	-	32	111	30,7
BisGMA:LLA	1:30	-	42	-	-
BisGMA:LLA[d]	1:30	-	36	138	43,4

[a] glass transition temperature - temperature at turning point

[b] melting point - temperature at peak maximum

[c] heat of fusion

[d] after annealing at 90 C for four hours

An increasing concentration of LLA results in a higher T_g, whereas increasing amounts of VL or CL result in lower T_g (see Table 6). Both lactones, VL and CL, act as softeners. They influence the glass transition behaviour in the same manner. The macromonomers of the molar composition BisGMA:VL:LLA of 1:2:6 or 1:2:10 and oligo(CL-co-LLA) macromonomers of the equal molar composition have T_g of almost the same magnitude. Cooligo(lactone) macromonomers, prepared by parallel or step reaction do not show clear distinctions in their glass transition temperatures. Macromonomers consisting of LLA and BisGMA in a molar ratio lower than 15 to 1 are amorphous. Higher contents of LLA yield partially crystalline oligomers, but only after annealing at 90 C. An annealing time of four hours is sufficient to accomplish the maximum heat of fusion and the maximum of crystallinity, respectively. The crystallisation behaviour of oligo(L-lactide) macromonomers is dependent on the thermal treatment. Amorphous macromonomers are obtained by fast cooling of the reaction products, whereas annealing results in partially crystalline oligo(L-lactide) macromonomers already at lower oligomerisation degrees than described in [13].

Conclusions and preview

Cooligo(lactone) macromonomers can be prepared by two reaction ways, by parallel or by step reaction. Making use of these two reaction procedures it is possible to synthesise cooligo(lactone) macromonomers with different microstructures, which cause different properties of the macromonomers. Poly(propyleneglycol) standards used for the SEC calibration leads to more realistic data of the molecular weights of these macromonomers than poly(styrene) standards as applied in [13].

Copolymerisation of these macromonomers with a diluting monomer, like tri(ethyleneglycol) dimethacrylate, can yield crosslinked polymers available as a matrix for biodegradable composites. The differences in the microstructure of the macromonomers may influence the properties of these copolymers as well as their degradation behaviour. The preparation and the characteristics of these copolymers are the subject of further investigations.

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