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Hyperbranched Polylactide Copolymers

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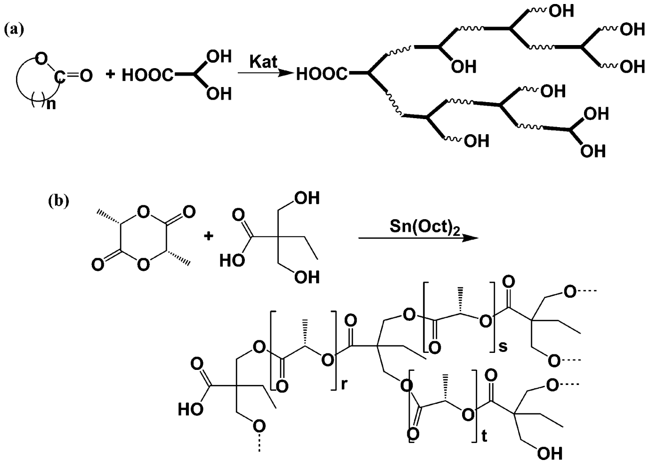
ABSTRACT: A series of hyperbranched poly(L-lactide) (PLLA) copolymers were prepared by copolymerization of dilactide with 2,2-bis(hydroxymethyl)butyric acid (BHB) as an AB_2 comonomer via a combined ring-opening polymerization/AB_2 polycondensation. Stannous 2-ethylhexanoate was used as a catalyst. Apparent molecular weights determined by size exclusion chromatography (SEC) (polystyrene standards) were in the range of 700−60 000 g/mol, decreasing with the degree of branching (DB). All branched copolyesters showed monomodal molecular weight distributions with low apparent polydispersities (SEC) in the range of 1.3−2.2. The branched comonomer was randomly incorporated in the copolyesters (^{13}C and ^1H NMR), thereby varying the DB. The degree of crystallization of the materials decreases with increasing DB. With more than 7% incorporation of the BHB monomer, amorphous materials were obtained (differential scanning calorimetry (DSC)). Solubility and solution viscosity depended strongly on the DB.

Introduction

Poly(L-lactide) (PLLA) is a linear aliphatic polyester and thermoplastic that is usually prepared by ring-opening polymerization (ROP) of L-lactide. PLLA is a biodegradable and bioadsorbable polymer that also possesses good biocompatibility. Therefore, PLLA has been studied intensely with respect to biomedical application in surgery, e.g., for surgical sutures, drug delivery systems, and internal bone fixation.[1−4] PLLA is also discussed as a promising bioerodible material for a wide range of commodity applications.[5,6] Most applications discussed at present require tailoring of the properties of PLLA, such as to reduce the crystallinity or melt viscosity. This is achieved, e.g., by copolymerization of diglycolide, ϵ-caprolactone, *meso*-lactide, or other comonomers.[6−8] Recently, an alternative strategy to generate unusual rheological and mechanical properties combined with a modified biodegradation profile has been recognized: the introduction of dendritic branching. For PLLA, a variety of branched molecular architectures has been reported, e.g., long-chain branched, grafted, star-shaped, dendritic, and/or cross-linked PLLA.[9−14]

Although hyperbranched polyesters have been the subject of numerous publications and represent a particularly important class of materials of interest for specialty coatings, nanostructured networks, and various biomedical applications,[15−17] only two syntheses of polylactide-based dendritic structures have been reported to date.[12,13] In elegant work, Hedrick and co-workers introduced a new class of polymer architectures, denoted "dendrimer-like star polymers".[18] They combined aspects of dendrimer synthesis with star polymer synthesis. Starting from a central core, these authors prepared these polymers by a divergent growth approach with the repetitive ROP of cyclic ester monomers, followed by functionalization and deprotection of an AB_2 branching point. On the basis of this concept, Hedrick et al. were also able to obtain hyperbranched aliphatic polyesters via polymerization of protected AB_x macromonomers.[12,19] Ouchi et al. recently reported the synthesis of long-chain branched polylactide copolymers via a one-pot copolymerization of lactide with mevalonolactone as a branching inimer.[13] However, no concepts for a systematic variation of the degree of branching have been reported to date.

Scheme 1. (a) General Scheme of the Synthetic Strategy, Based on the Combination of Ring-Opening Polymerization and AB_2 Polycondensation; (b) Copolymerization of L-Lactide and 2,2′-Bis(hydroxymethyl)butyric Acid, i.e., the Synthetic Route Employed for the Preparation of Dendritic Copolyesters



In a recent work we described an enzymatic route toward hyperbranched aliphatic polycaprolactone copolyesters, based on the combination of ROP and polycondensation of AB_2 monomers.[20] Bis(hydroxy)carboxylic acids were employed as branching AB_2 comonomer units. The hydroxyl groups both must act as initiator for the ROP of the cyclic AB monomer and take part in the copolycondensation steps. A general scheme of the branching ROP copolycondensation is shown in Scheme 1a.

In the current paper we use the combined AB_2-ROP/polycondensation for the metal-catalyzed bulk synthesis of hyperbranched polylactide copolyesters, employing stannous octanoate ($Sn(Oct)_2$) as catalyst. $Sn(Oct)_2$ is preferred for the bulk polymerization of lactide due to its solubility in molten lactide, high catalytic activity, and the low rate of racemization of the polymer[6] and its acceptance by the FDA as a food additive. Polymerization of lactide with $Sn(Oct)_2$ has been reported in numerous papers and is generally described as a coordination−insertion mechanism with ring opening of the lactide, resulting in the addition of two lactid acid molecules to the growing end of the polymer chain.[7,21,22]

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Table 1. Characterization Data of the Dendritic Copolylactide Samples

		BHB (mol %)				SEC[c]	
copolymer	L-La (mol %) (feed)	feed	polymer[a]	DB[b]	yield (%)	M_n (g/mol)	M_w/M_n
PLLA-100	100	0	0	0	92	57500	1.95
PLLA-99	99	1	0.9	0.018	80	19900	1.85
PLLA-98	98	2	2.2	0.042	84	12200	1.75
PLLA-97	97	3	3.1	0.058	72	8800	1.59
PLLA-96	96	4	4.1	0.076	57	9400	1.41
PLLA-95	95	5	5.1	0.092	62	7600	1.36
PLLA-92	92	8	11.8	0.189	80	1800	2.42
PLLA-90	90	10	16.8	0.246	79	1300	2.11
PLLA-85	85	15	22.1	0.296	36	800	1.96
PLLA-80	80	20	27.6	0.339	51	900	1.48
PLLA-75	75	25	31.3	0.363	36	650	1.55
PLLA-50	50	50	60.2	0.469	41	270	1.09

[a] Calculated from ^{1}H NMR spectra. [b] According to the definition of Hölter et al.[21] [c] SEC measurements in $CHCl_3$ (polystyrene standards).

As shown in Scheme 1b, L-lactide has been employed as cyclic AB monomer and 2,2-bis(hydroxymethyl)butyric acid (BHB) was used as AB_2 comonomer. This was expected to result in dendritic copolyesters. By systematic variation of the fraction of the AB_2 comonomer, a series of long-chain branched and hyperbranched copolyesters with different degree of branching (DB) have been prepared and studied with respect to their properties.

Experimental Section

Materials. L-Lactide (98%, Aldrich Chemical Co., L-LA) was recrystallized from acetone before use. 2,2-Bis(hydroxymethyl)butyric acid (98%, Aldrich Chemical Co., BHB) was dried in a vacuum over dry silica gel for 24 h prior to use. Stannous(II) 2-ethylhexanoate (95%, Aldrich Chemical Co., $Sn(Oct)_2$) was used as received. All solvents were of analytical grade and used as received.

Polymerization. The branched polylactide copolyesters were prepared via bulk copolymerization of L-LA and BHB, using $Sn(Oct)_2$ as catalyst (molar ratio of L-LA/catalyst = 1000). For systematic investigation of the polymerization and variation of the conditions a "carousel reaction station" for parallel synthesis with gastight closed glass tubes was used. Since the polymerization varied slightly with composition, the synthesis is described for two different samples.

Copolymerization of L-LA and BHB (Exemplified for Sample PLLA-95). L-LA (2.883 g, 20.0 mmol) and BHB (0.156 g, 1.05 mmol) were molten at 120 °C. $Sn(Oct)_2$ (0.007 mL, 0.02 mmol), as a 10 vol % solution in toluene, was added to the clear melt. After 24 h the reaction mixture was allowed to cool to room temperature. The solid product was dissolved in $CHCl_3$ (20 mL) and poured into methanol to precipate the branched polymer. The product was isolated by filtration and dried in a vacuum for 48 h to yield 1.88 g (61.8%) of a white powder. ^{1}H NMR: δ 5.23−5.10 (OOCC*H*(CH$_3$)O); 4.49−4.08 (OOCC(CH$_2$CH$_3$)(C*H*$_2$O)); 1.70 (OOCC(C*H*$_2$CH$_3$)(CH$_2$O)); 1.63−1.46 (OOCCH(C*H*$_3$)O); 1.27 (OOCC(C*H*$_2$CH$_3$)(CH$_2$O)); 0.92 (OOCC(CH$_2$C*H*$_3$)(CH$_2$O)). ^{13}C NMR: δ 175.3 (OO*C*C(CH$_2$CH$_3$)(CH$_2$O)); 169.7 (OO*C*CH(CH$_3$)O); 69.2 (OOC*C*H(CH$_3$)O); 66.8 (OOCC(CH$_2$CH$_3$)(*C*H$_2$O)); 50.1 (OOC*C*(CH$_2$CH$_3$)(CH$_2$O)); 20.6 (OOCC(*C*H$_2$CH$_3$)(CH$_2$O)); 16.8 (OOCCH(*C*H$_3$)O); 8.1 (OOCC(CH$_2$*C*H$_3$)(CH$_2$O)).

Copolymerization of L-LA and BHB (Exemplified for Sample PLLA-75). L-LA (2.883 g, 20.0 mmol) and BHB (0.988 g, 6.67 mmol) were molten at 120 °C. $Sn(Oct)_2$ (0.007 mL, 0.02 mmol), as a 10 vol % solution in toluene, was added to the clear melt. After 24 h the reaction mixture was allowed to cool to room temperature. The solid product was dissolved in $CHCl_3$ (20 mL) and washed three times with 30 mL of deionized water. The solution was then dried over anhydrous sodium sulfate, filtered, and concentrated and dried in a vacuum to yield 1.39 g (35.8%) of a clear colorless oil. ^{1}H NMR: δ 5.4 (O*H*); 5.23−5.10 (OOCC*H*(CH$_3$)O); 4.49−4.08 (OOCC(CH$_2$CH$_3$)(C*H*$_2$O)); 3.81−3.59 (C*H*$_2$OH) 1.70 (OOCC(C*H*$_2$CH$_3$)(CH$_2$O)); 1.63−1.46 (OOCCH(C*H*$_3$)O); 1.27 (OOCC(C*H*$_2$CH$_3$)(CH$_2$O)); 0.92 (OOCC(CH$_2$C*H*$_3$)(CH$_2$O)). ^{13}C NMR: δ 175.3 (OO*C*C(CH$_2$CH$_3$)(CH$_2$O)); 169.7 (OO*C*CH(CH$_3$)O); 69.2 (OOC*C*H(CH$_3$)O); 66.8 (OOCC(CH$_2$CH$_3$)(*C*H$_2$O)); 63.7 (*C*H$_2$OH); 50.1 (OOC*C*(CH$_2$CH$_3$)(CH$_2$O)); 20.6 (OOCC(*C*H$_2$CH$_3$)(CH$_2$O)); 16.8 (OOCCH(*C*H$_3$)O); 8.1 (OOCC(CH$_2$*C*H$_3$)(CH$_2$O)).

Characterization. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ using a Bruker ARX 300 spectrometer at 300 and 75.4 MHz, respectively. Size exclusion chromatography (SEC) of the samples was carried out using a Knauer system with refractive index (RI) detector under the following conditions: Microgel set A22 10 μm columns—combination consisting of four columns (100, 1000, 10^4, 10^5 Å); $CHCl_3$ as the eluent at a flow rate of 1 mL/min; concentrations of 6−10 mg/mL. The calibration curve was obtained using linear polystyrene (PS) standards. All measurements were carried out at 35 °C. Vapor pressure osmometry (VPO) was carried out using a Knauer vapor pressure osmometer K7000 in $CHCl_3$ in the concentration range 10−40 mg/mL at 30 °C. Benzil was used for calibration. The thermal properties were measured by differential scanning calorimetry (DSC) using a Perkin-Elmer 7 Series Thermal Analysis System in the range of −50 to 200 °C at heating rates of 36, 25, 16, and 9 K/min. The melting point of indium (156 °C) was used for calibration. The T_g was determined as the midpoint of the heat capacity increase of the second heating process and T_m as the endothermal peak in the DSC curve of the second heating process. Viscosimetry was performed with a LAUDA automated viscosimeter PVS1, using $CHCl_3$ as the eluent at a temperature of 25 °C.

Results and Discussion

All copolymerization reactions of L-lactide (L-LA) and 2,2-bis(hydroxymethyl)butyric acid (BHB) were carried out at 120 °C for 24 h in bulk, using $Sn(Oct)_2$ as catalyst, which catalyzes both ROP and the concurrent polycondensation of the AB_2 monomer BHB. This is a prerequisite for the formation of the desired hyperbranched copolymer structure. The selection of BHB as branching AB_2 unit was based on its slightly lower polarity than the commonly used 2,2-bis(hydroxymethyl)propionic acid, also employed in the studies discussed in the Introduction, as well as its good solubility in the melt of the dilactide. In this context, also the melting temperature of 120 °C, i.e., below the reaction temperature, played an important role. By systematic variation of the fraction of the AB_2 comonomer, a series of long-chain branched and hyperbranched polylactide copolymers with systematically varied degree of branching (DB) have been prepared. The sample nomenclature uses the following terminology: PLLA-*X* where *X* corresponds to the molar amount of L-lactide in the monomer feed. The results of all copolymerizations are summarized in Table 1.

^{1}H NMR spectra for the series of PLLA-based copolyesters of different DB (degree of branching) are shown in Figure 1,

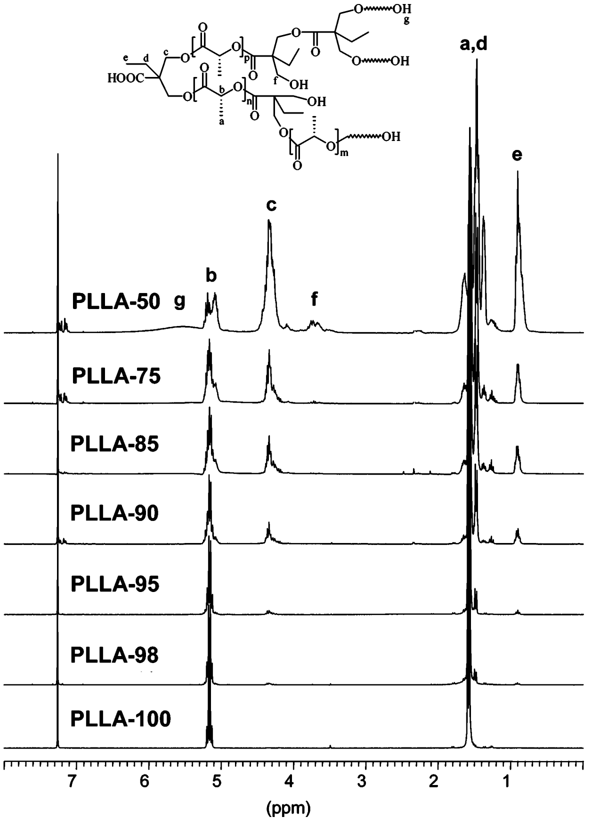

Figure 1. ^{1}H NMR spectra of copolyesters of L-lactide and 2,2-bis-(hydroxymethyl)butyric acid (BHB) containing different amounts of BHB.

confirming incorporation of the AB$_2$ comonomer BHB. Obviously, the DB of the hyperbranched copolymers can be controlled by the monomer ratio in the feed. With increasing amount of the comonomer BHB in the copolyester the resonances of the L-LA units (5.2 and 1.6 ppm) show an increasingly complex splitting pattern, which is caused by the polymer microstructure; i.e., an increasing amount of combinations between L-LA and BHB units is present.

Another important issue is whether the branched comonomer is homogeneously incorporated over the whole molecular weight distribution of the hyperbranched polylactide copolymers. Unfortunately, well-resolved MALDI-TOF spectra of the different fractions of the distribution were not obtained, which would permit a conclusion on this. However, formation of hyperbranched BHB homopolymers was clearly not observed, as it is obvious from the excellent solubility of the products in CHCl$_3$. This is in contrast to the insolubility of hyperbranched BHB homopolymers in CHCl$_3$, as shown in a detailed solubility study. In addition to this observation, the gradual change of the polymer properties (vide infra) with increasing incorporation of branched BHB supports random copolymerization of BHB with dilactide.

The fraction of AB$_2$ comonomer incorporated was determined from the respective ^{1}H NMR signal intensity. The BHB units incorporated show characteristic resonances at 4.3 and 3.7 ppm that can be used to quantify their fraction by comparison with the resonance of the (−OOC−CH) group of the L-LA units located at 5.2 ppm. The fraction of BHB incorporated in the hyperbranched copolymers corresponded to the monomer feed up to an amount of 7% BHB. For higher amounts of BHB, the incorporation in the copolymers exceeded the monomer fraction in the feed. One possible reason for this behavior could be that compounds containing free hydroxyl groups, like e.g., water or hydroxy acids, are employed to control the reaction rate and to regulate the average molecular weight of linear PLLA and may have a similar effect for the hyperbranched structure.[2] However, polymerization under strict water removal conditions showed no significant effect on the degree of incorporation of BHB or molecular weights, as discussed below. The DBs for the copolymers were in the range of 0.02−0.47, according to the definition for AB/AB$_2$ copolymers reported by Hölter et al. (eq 1):[23]

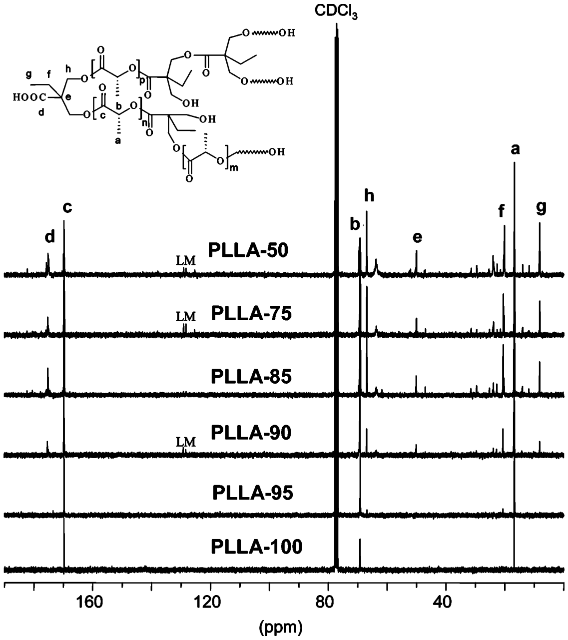

Figure 2. ^{13}C NMR spectra of copolyesters of L-lactide and 2,2-bis-(hydroxymethyl)butyric acid (BHB) containing different amounts of BHB.

$$\mathrm{DB}^{\mathrm{stat}}_{\mathrm{AB/AB_2}} = 2\,\frac{1 - x_{\mathrm{AB}}}{(2 - x_{\mathrm{AB}})^2} \tag{1}$$

where x_{AB} is the molar fraction of AB monomer.

A kinetic study of the copolymerization using 5 mol % BHB showed that incorporation of the comonomers was analogous to the AB/AB$_2$ monomer ratio in the feed. In these kinetic experiments, integration of the ^{1}H NMR spectra showed (1−24 h) an incorporation of BHB of 4.8−5.3% at any time.

In addition to ^{1}H NMR data, ^{13}C NMR spectroscopy (Figure 2) also evidences random incorporation of the AB$_2$ comonomer BHB; i.e., the presence of several resonances between 175 and 180 ppm is clearly due to ester groups in slightly different microenvironments. When the incorporation of BHB exceeds 20%, a low-intensity signal at 182 ppm is observed, which reveals the presence of a free carboxylic acid group at the focal monomer unit. For higher amounts of BHB in the copolymer the intensity of this signal increases. This is explained by the decrease of molecular weights with increasing DB, which is analyzed in the subsequent section.

Under the reaction conditions employed, homopolymerization of BHB resulted in low molecular weight oligomers only, which are soluble in methanol and insoluble in chloroform. On the basis of this result, it is reasonable to assume that sequences of at maximum two or three BHB units are present in the copolyesters. Apart from this limitation, NMR data indicate that the incorporation of the different monomer units in the copolymers is random.

Table 2. Thermal Properties of Selected Dendritic Copolylactide Samples

copolymer	T_g (°C)	T_m (°C)	ΔH (J/g)
PLLA-100	62.5	175.6	53.1
PLLA-99	56.9	165.4	44.4
PLLA-98	52.8	156.7	29.2
PLLA-97	50.1	147.1	32.5
PLLA-96	50.2	142.9	38.6
PLLA-95	49.1	142.9	9.5
PLLA-92	20.6		
PLLA-90	18.0		

The data shown in Table 1 illustrate that both yields and molar masses of the hyperbranched copolyesters exhibit a strongly decreasing tendency with increasing ratio of AB_2 comonomer BHB. PLLA copolyesters containing up to 6% BHB can be precipitated in methanol. For higher amounts of BHB, no precipitation was observed, most probably due to the lack of crystallinity. Consequently, we modified the purification protocol and extracted the chloroform solution with deionized water. Most probably, the increase in the number of hydroxyl end groups with increasing DB leads to improved solubility in methanol. In summary, the decrease of the degree of crystallization and of the T_gs of the higher branched PLLA copolyesters leads to a decrease of the fraction of the material that can be obtained by precipitation.

Apparent molecular weights determined by means of SEC (PS standards) were in the range of 700−60 000 g/mol, decreasing with the DB. All branched copolyesters showed monomodal molecular weight distributions with low apparent polydispersities (SEC) in the range of 1.3−2.2. Since the hydrodynamic volume of branched polymers is a function of the DP_n, the degree of branching, and possible solvent/polymer interactions, SEC calibration with commonly used linear PS standards is problematic. The differences between the hydrodynamic volume of the hyperbranched sample and the linear standard is known to lead to underestimated molecular weights. On the other hand, hyperbranched polymers often exhibit aggregation or interaction with the SEC columns and solvent due to their large number of end groups. This can lead to overestimated molecular weights. To verify which effect dominates in the SEC measurements, it is necessary to compare the data with results from other methods. VPO measurements are independent of the structure of the samples; i.e., this method is suitable for the determination of molecular weights of hyperbranched samples. On the other hand, VPO is highly sensitive to traces of low molecular weight impurities. VPO characterization for a carefully dried sample PLLA-90 indeed revealed a molecular weight of 1800. This result suggests that SEC leads to underestimated molecular weights. A more detailed study of the measurement error with regard to molecular weight is in progress.

From a materials research point of view, the effect of dendritic branching on melting point, glass transition, and crystalline fraction represents a key issue for further processing and applications. The thermal properties of the hyperbranched polylactide copolymers have been characterized by DSC. As expected, the incorporation of small fractions of BHB resulted in a decrease of the melting point, melting enthalpy ΔH_m, and the T_g (Table 2). BHB fractions exceeding 6% led to the formation of fully amorphous materials that were obtained as highly viscous, sticky liquids.

Compared to poly(L-lactide-*co*-*meso*-lactide),[6] the melting point of the branched polylactide copolyesters decreased more rapidly with comonomer content (Figure 3).

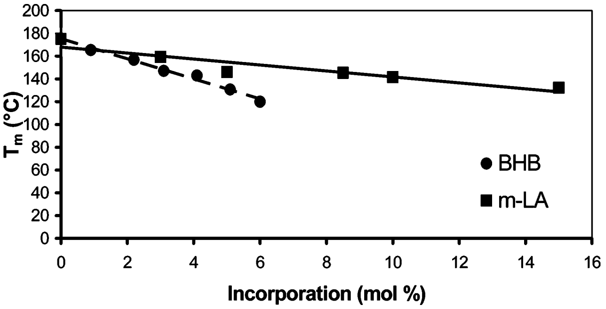

Figure 3. Comparison of the influence of 2,2-bis(hydroxymethyl)-butyric acid (BHB) and *meso*-lactide (*m*-LA) on the melting point of copolylactides.

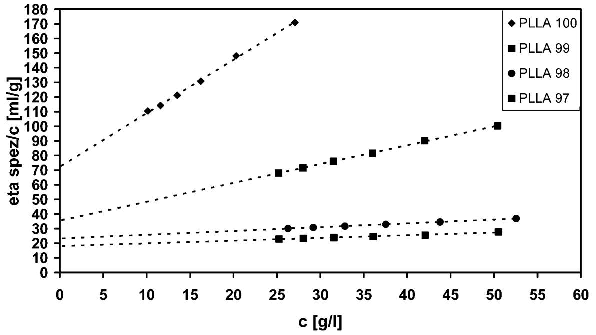

Figure 4. Reduced viscosity value η_{sp}/c vs concentration of linear and long chain branched polylactide copolyesters.

Specific and intrinsic viscosities [η] of the PLLA copolymers in $CHCl_3$ have also been measured. In all cases the intrinsic viscosities of the dendritic copolyesters were significantly lower than for their linear analogue (Figure 4). Interestingly, even at low degrees of branching (1−3% BHB), already a strong decrease of specific and intrinsic viscosity was observed, even though molecular weights of these materials do not show a strong decrease in comparison to the linear homopolymer. These findings point to a more compact/dense structure of the hyperbranched copolyester in contrast to the open coil conformation for linear PLLA. For higher degrees of branching the specific and intrinsic viscosity in $CHCl_3$ did not decrease to a stronger extent. This may represent an important finding with respect to processing of branched polylactides. It should be mentioned that the viscosity decrease observed is due to both the decrease in molecular weight and the increasingly branched structure, as is obvious from a comparison with linear samples of similarly low molecular weight.

Conclusion

The combination of the ROP of L-LA with the polycondensation of BHB can be exploited to prepare hyperbranched polylactide copolyesters. To the best of our knowledge, this represents the first case of a one-pot copolymerization of lactides with an AB_2 monomer to branched polylactides. This synthetic route permits to control the degree of branching (DB) by the AB/AB_2 comonomer ratio. Variation of the DB permits to adjust the thermal and rheological properties of the materials. Reactions run on larger scale (100 g) showed promising results with respect to convenient scale-up of the procedure. A systematic study concerning the application of the synthetic principles described here to other, structurally similar monomers is in progress as well as variation of the synthetic conditions to enhance molecular weights at higher degrees of branching. In addition, blending of the hyperbranched polylactides with their linear analogues shows interesting effects that may offer processing advantages. The results of this study will be reported in due course.

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