

THERMAL PROPERTIES AND CRYSTALLIZATION BEHAVIOR OF HYPERBRANCHED POLY (ϵ -CAPROLACTONE) COPOLYESTERS

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Abstract. Series of hyperbranched poly(ϵ -caprolactone)s with different degree of branching (DB) and molecular weights were obtained by enzymatic synthesis, based on the combination of concurrent ring-opening polymerization of ϵ -caprolactone and polycondensation of 2,2'-bis(hydroxymethyl)butyric acid. The hyperbranched polymers were studied with respect to molecular weights, DB, thermal properties, crystallization behavior and morphology.

Key words: hyperbranched poly(ϵ -caprolactone), degree of branching, thermal properties, crystallization degree, morphology

INTRODUCTION

Hyperbranched macromolecules experience considerable and increasing interest in polymer science, due to their potential as new materials in e.g., biomedical applications, packaging and environmental protection¹. Compared with dendrimers obtained from multistep synthesis, hyperbranched polymers are advantageous, as they can be conveniently synthesized via one-step polymerization processes². These highly branched macromolecules are characterized by a globular structure and exhibit different properties from those of linear polymers of the same molar mass, such the absence of entanglements in the solid state³. They are being considered for use in advanced coatings⁴, drug delivery and release⁵, for surface modification and as additives for polymer processing as rheological modifiers⁶.

Particular interest is currently placed on biocompatible or biodegradable hyperbranched polymers, such as aliphatic polyesters, due to their potential as new materials in biomedical and pharmaceutical applications, packing and environmental protection⁷. Extensive studies on the biodegradability of traditional linear aliphatic

polyesters [i.e., poly (D,L-lactide, polyglycolide, and poly(ϵ -caprolactone)] have been reported. Consequently, we have become interested in the synthesis of hyperbranched polyesters based on ϵ -caprolactone⁸.

To date, no systematic studies on the variation of the degree of branching of crystallizable polymers have been reported. Based on the synthetic methodology presented in a short Communication previously⁹, a series of HB-PCL with different degree of branching (DB) have been obtained via concurrent ring-opening polymerization (ROP) and polycondensation of ϵ -caprolactone (ϵ -CL) as AB monomer and 2, 2'-bis(hydroxymethyl)butyric acid (BHB) as branching AB₂ comonomer units. The hyperbranched polymers were analyzed with respect to molecular weights, DB, thermal properties, crystallization behavior and morphology. Linear poly(ϵ -caprolactone) (L-PCL) has been used for comparison.

Experimental part

Materials. ϵ -CL (99%, Aldrich) was dried over CaH₂, distilled under reduced pressure and collected under argon atmosphere. BHB (98%, Aldrich) was dried in vacuum over dry silica gel for 24 h prior to use. Novozym 435, supported *Lipase B* from *Candida Antarctica*, was obtained from Novozymes company. Toluene was distilled over CaH₂ under argon and stored over molecular sieves. Chloroform (CHCl₃) and tetrahydrofuran (THF) were used as received. Linear poly (ϵ -caprolactone) (L-PCL), CAPA 6500 was kindly provided by Solvay Caprolactones (United Kingdom).

Synthesis of HB-PCL. By systematic variation of the BHB fraction in the feed, six HB-PCL samples with different DB have been synthesized as reported in the previous paper⁹. The structural verification by assignment of the ¹H-NMR signals is in accordance with the results published previously: ¹H-NMR (CDCl₃): δ = [4.26 (-O-CH₂C(CH₂)CO-)*; 4.02 (-O-CH₂-CH₂-); 3.70 (HO-CH₂-)*; 2.27 (-O-CO-CH₂-CH₂); 1.61 (-O-CO-CH₂-CH₂-CH₂-)*; 1.34 (-CH₂-CH₃)*; 0.89 (-CH₂-CH₃)*] ppm. ¹³C-NMR (CDCl₃): δ = [176.36 (HOOC-C(CH₂OH)(CH₂-CH₃)COOH); 172.93-173.61 (-CH₂-O-CO-CH₂-); 64.10 (-O-CH₂-CH₂-); 62.43 (-OCH₂-C(CH₂OH)(CH₂-CH₃)COOH)*; 49.73-51.73 (-OCH₂-C(CH₂OH)(CH₂-CH₃)COOH)*; 32,10 (-OC-O-CH₂-CH₂); 28.24 (-CH₂-CH₂-CH₂-O-); 26 (-O-CO-CH₂-CH₂-); 24.48 (-CH₂-CH₂-CH₂-); 23.33 (-CH₂-CH₃)*; 8.25 (-CH₂-CH₃)*] ppm (* peaks that correspond to the branching unit).

Instrumental analysis. ¹H-NMR and ¹³C-NMR spectra were recorded in *d*-chloroform using a Bruker ARX 300 spectrometer operating at 300 and 75.4 MHz, respectively. Molecular weights were determined by gel permeation chromatography (GPC), carried out on a PSS system with RI and UV detectors, using PSS-SDV columns and CHCl₃ as the eluent at a flow rate of 1 mL/min (polystyrene (PS) standards for calibration) and by vapor pressure osmometry (VPO), using a Knauer vapor pressure osmometer, K 7000, in toluene at 85°C, in the concentration range of 10-40 mg/ml. (benzil for calibration). Thermal properties were determined by differential scanning calorimetry (DSC), using a Perkin Elmer 7 Series Thermal Analysis System, in the temperature range of -100°C to 100°C, at four different heating rates: 9, 16, 25 and 36 K/min. Wide angle X-ray scattering (WAXS) profiles were taken at room temperature, using a Siemens D500 wide-angle X-ray powder diffractometer apparatus with CuK α used as the radiation source. Polarizing light

photomicrographs were taken with a Zeiss Axioplan 2 microscope equipped with digital camera.

Results and discussion

Analyzing the results presented in Table 1, it can be noticed that the yield of hyperbranched copolyesters records a decreasing tendency with increasing comonomer fraction in the feed (BHB_{th}). The fraction of incorporated BHB in HB-PCLs (BHB_{exp}), calculated from the integration of 1H -NMR signals, is somewhat lower than BHB_{th} (Table 1).

Molecular weight characterization of hyperbranched polymers possessing a large number of hydroxyl end groups often leads to erroneous results, if size exclusion chromatography with common linear standards is employed¹⁰, leading to considerable overestimation of molecular weights¹¹. Table 1 shows that the molecular weights of the synthesized HB-PCLs, measured by means of GPC and VPO, exhibit a slightly decreasing tendency with increasing BHB fraction. There is a striking difference between the molecular weights determined by GPC and VPO, as observed also for hyperbranched polyethers in previous work.¹² Nevertheless, all copolyesters prepared show monomodal molecular weight distributions and relatively low polydispersities that lead to the conclusion that the formation of aggregates does not seem to be very likely under GPC conditions. VPO is independent of polymer structure and thus more suitable for determination of molecular weights of hyperbranched polymers¹². All samples show excellent linear correlation in the VPO measurements. Hence, aggregation due to polar hydroxyl groups can be excluded. However, VPO is a colligate method, i.e. the presence of traces of solvents will have a strong effect on molecular weights measured. Thus, VPO rather under- than overestimates molecular weights.

The degree of branching (DB_{th}) and the number-average length of linear segments between two branching points (DP_s) give information concerning the global topology of the hyperbranched polymers and may be calculated as following¹³:

$$DB_{th AB/AB_2} = \frac{2D}{2D + L_{co}} \quad (1)$$

$$DP_s = \frac{L_{co}}{D + T_{co}} = \frac{1}{2} \cdot \frac{(r^2 + 2r + 2)}{r + 1} \quad (2)$$

where: D - dendritic units; L_{co} - total number of linear units in the AB/AB₂ copolymers; T_{co} - total number of terminal units; r defines the monomer ratio AB/AB₂.

Sample	BHB _{th}	BHB _{exp}	Yield	GPC			VPO
	[mol%]	[mol%]		M _n	M _w	M _w /M _n	M _n
			[%]	[g/mol]	[g/mol]		[g/mol]
L-PCL	-	-	-	62,000	100,270	1.61	-
HB-PCL1	1	0.9	90	8,950	20,150	2.1	2,023
HB-PCL2	2	1.9	95	7,165	14,540	2	1,746
HB-PCL6	6	4.4	97	3,540	6,260	1.76	1,706
HB-PCL10	10	8.3	85	2,520	4,096	1.62	1,417
	15	11.3	80	2,490	4,250	1.7	1,351
HB-PCL15	25	20	73	1,070	1,204	1.12	1,208
HB-PCL25							

Table 1

Characterization data of the synthesized HB-PCL samples

For the series of HB-PCLs, DB_{th} is in the range of 1.9 to 33.6, increasing with the amount of BHB comonomer incorporated. For all HB-PCLs we obtained DB_{exp} lower than DB_{th} (Table 2). The values for DP_s depend on the incorporated monomer ratio AB/AB₂ and vary between 2.1 and 50.5. These values decrease with increasing fraction of BHB_{exp} (Table 2).

Typical DSC diagrams for the series of samples obtained upon heating are shown in Fig. 1. All DSC diagrams of HB-PCLs show a characteristic double endotherm, from which the more intensive upper part was confirmed by optical microscopy to be the actual melting point. The melting temperature (T_m) is reported as the peak of the melting endotherms. All of the HB-PCL samples showed melting endotherms. However, molecular weights and degree of branching strongly influence crystallization and melting (Table 2). An increase of BHB_{exp} values from 0.9 to 20 mol % causes a decrease of melting points from 54.6 to 30.9°C (Figure 5). Correlating T_m with DP_s of the HB-PCLs, it can be observed that T_m is determined by the average length of the linear ε-CL segments between branch points, lowering its values with decreasing DP_s. The heat of fusion reflects the crystalline fraction. A decreasing trend with increasing incorporation of branching comonomer can be seen.

The degree of crystallization X_c of L-PCL and HB-PCLs was calculated according to the relation (3) (Table 2).

$$X_c(\%) = (\Delta H_f / \Delta H_f^0) \cdot 100 \quad (3)$$

where: ΔH_f - measured heat of fusion for the sample; ΔH_f⁰ - heat of fusion for 100% crystalline

L-PCL (ΔH_f for crystalline L-PCL is 3.69 kcal/mole or 135 J/g)¹⁴.

Sample	BHB _{exp} [mol %]	DB _{th} [mol%]	DB _{exp} [mol%]	DP _s	T _g [°C]	T _m [°C]	ΔH_m [J/g]	X _c [%]
L-PCL	0	0	0	100	-54.2	59.6	65.4	48.4
HB-PCL1	0.9	1.9	0.9	50.5	-50.8	54.6	73.1	54.2
HB-PCL2	1.9	3.9	3.8	29.3	-56	54.2	74.7	55.3
HB-PCL6	4.4	11.3	8.4	11	-52	52.1	71.3	52.8
HB-PCL10	8.3	14.2	10.7	5.9	-46.5	45	61.2	45.3
HB-PCL15	11.3	26.08	20.2	3.60	-59.3	38.4	50	37
HB-PCL25	20	40	33.6	2.12	-59.1	30.9	12.3	9.1

Table 2
DB_{th}, DB_{exp}, DP_s and thermal properties of the HB-PCLs

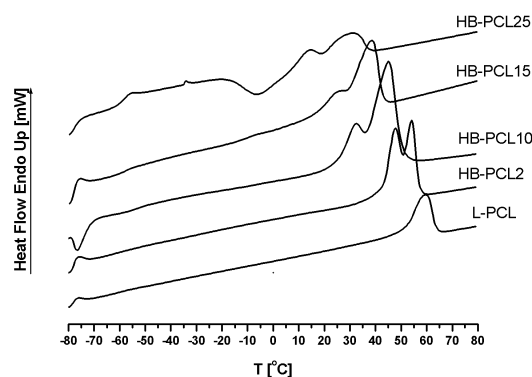


Fig. 1- DSC diagrams upon heating for L-PCL and HB-PCLs.

Intuitively, one may assume that the hyperbranched polymers show a lower tendency to crystallize than the linear analog. Surprisingly, three of HB-PCL samples (with DB_{exp} below 8.4) exhibited even higher degree of crystallization than L-PCL. The highest value for X_c and for the melting enthalpy was found for HB-PCL2 that slightly differs from HB-PCL1 value (Table 2). One possible explanation for this unexpected finding is that the chain ends of the hyperbranched structure lead to an enhanced mobility that permits an alignment of linear segments, increasing in this way the degree of crystallization. Furthermore, the absence of entanglements for the long-chain branched copolymers in

combination with the lowered molecular weight is likely to affect crystallization kinetics, leading to accelerated crystallization.

The WAXS profiles (not shown here) show that all HB-PCLs synthesized with DB_{exp} up to 33.6 form crystalline regions, as also confirmed by DSC.

As expected, the degree of crystallization of the polyesters decreases with increasing DB. The L-PCL shows an intense reflection at $2\theta = 21.1^\circ$ (corresponding to $d = 4.19 \text{ \AA}$) and two smaller ones at 21.7° (4.09 \AA) and 23.5° (3.78 \AA). This WAXS profile is ascribed to the orthorhombic unit cell of L-PCL ($a = 7.46 \text{ \AA}$; $b = 4.97 \text{ \AA}$; $c = 17.29 \text{ \AA}$), which is perpendicular to the chain direction¹⁵. The hyperbranched polyester HB-PCL2 (with $DB_{exp} = 3.8$) exhibits four reflections, three of them with the same relative positions and intensity ratios as for L-PCL, but all shifted to lower diffraction angles (2θ : 20.6° , 20.9° and 21.8°), which according to Bragg's law correspond to larger d -spacing. Thus, the crystalline domains of the long-chain branched sample HB-PCL2 appear to be less compact in comparison to the linear analog. The intensity of the fourth diffraction peak (at $2\theta = 21.2^\circ$) is rather low, but one can notice that this reflection is present in all the WAXS profiles, regardless of the DB of the polyesters. The increasingly branched polyester samples HB-PCL10 and HB-PCL25 (with DB of 10.7 and 33.6, respectively) show four identical diffraction peaks at 2θ : 20° , 20.5° , 21.2° , and 22.2° . The angular positions of the two main peaks (with high diffraction intensities) correspond to d -spacings of 4.43 \AA and 4.00 \AA , respectively, and may suggest that in the case of medium and highly hyperbranched polyesters (with DB up to 33.6) there are two crystalline polymorphs with different compactness and different chain packing.

The crystalline morphology of the samples was investigated by light microscopy. The samples were molten, annealed for 5 minutes in the melt and then rapidly cooled to the crystallization temperature. Fig. 2 shows polarized optical micrographs for L-PCL ($T_c = 35.8^\circ\text{C}$) and HB-PCL10 ($T_c = 35.8^\circ\text{C}$). For L-PCL well-grown spherulites, which are very tightly spaced, are observed with the average radius much larger (200 \mu m size) than that of the HB-PCL samples (about 30 \mu m). It can be observed that the hyperbranched materials form less ordered, undeveloped spherulites with irregular shapes compared with those found for L-PCL. This morphology could be attributed to the lower content of crystallites of HB-PCLs compared with L-PCL as the incorporation of the core molecule disturbs crystal formation considerably. In addition, crystallization is slowed down considerably by incorporation of the branching units.

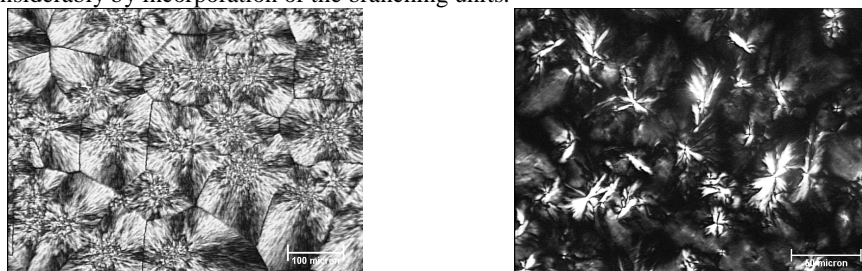


Fig. 2 - POM micrographs of isothermally crystallized poly(ϵ -caprolactone)s: L-PCL and HB-PCL10.

Because of the low degree of crystallization of the HB-PCLs, the spherulites, which normally contain all material, are not space filling and there is amorphous material between the spherulites. This indicates a slightly heterogeneous chemical composition of the hyperbranched material, and a phase separation in crystallizable and non-crystallizable material during the crystallization. That could also explain the double melting peak obtained in the DSC diagrams.

Conclusions

By systematic variation of the BHB fraction in the reaction feed, a series of HB-PCLs copolyesters with different DB has been obtained via enzymatic synthesis based on ROP/ polycondensation combination. The properties of these copolymers investigated by different methods were found to exhibit a strong dependence on the DB. The molecular weights of the synthesized HB-PCLs exhibit a decreasing tendency with increasing fraction of BHB. The calculated values for DP_s depend on the monomer ratio AB/AB_2 and decrease with increasing fraction of BHB. T_g , T_m and ΔH_m decreased with increasing content of the branching comonomer BHB, due to the expected increase of the amorphous fraction. Also, higher values of the DP_s corresponded to lower T_m in the HB-PCLs. The WAXS data show that all hyperbranched polymer samples exhibit crystalline fractions. In the case of the HB-PCLs, with DB up to 33.6, there were found two crystalline polymorphs with different compactness and different chain packing. POM micrographs showed for HB-PCLs a number of smaller, irregular shaped spherulites compared with the L-PCL ones. Because of the low degree of crystallization of the HB-PCLs it could be seen that there is amorphous material between the spherulites, indicating a slightly heterogeneous chemical composition of the HB material, and a phase separation in crystallizable and non-crystallizable material during the crystallization.

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