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Polymer 46 (2005) 5025–5031

polymer

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Chemical synthesis and characterization of POSS-functionalized poly[3-hydroxyalkanoates]

Roland Hany[a,*], René Hartmann[a,b,d], Christine Böhlen[a], Sandro Brandenberger[a], Jumpei Kawada[c,1], Christiane Löwe[a], Manfred Zinn[b], Bernard Witholt[d], Robert H. Marchessault[c]

[a] *Materials Science and Technology (Empa), CH-8600 Dübendorf, Switzerland*
[b] *Materials Science and Technology (Empa), CH-9014 St Gallen, Switzerland*
[c] *Department of Chemistry, McGill University, 3420 University St, Montreal, QC, Canada H3A 2A7*
[d] *Swiss Federal Institute of Technology Zürich (ETHZ), Institute of Biotechnology, ETH Hönggerberg HPT, CH-8093 Zürich, Switzerland*

Received 8 March 2005; received in revised form 8 April 2005; accepted 9 April 2005
Available online 28 April 2005

Abstract

A polyhedral oligomeric silsesquioxane containing seven isobutyl groups and one mercaptopropyl group (POSS-SH) was linked via a free radical addition reaction to the side-chain double bonds of bacterial poly[3-hydroxyalkanoate-*co*-3-hydroxyalkenoate], (PHAE). PHAE with 11.5, 55, 78, and 97 mol% of double bonds were used to produce a series of inorganic–organic hybrid materials, PHAE–POSS, with increasing amounts of POSS. The reactions proceeded with high yields and limited side reactions, confirmed with NMR and GPC experiments. X-ray diffraction and ^{13}C solid-state NMR analysis of these nanocomposite materials suggested the favoured crystallization of POSS, with PHAE functioning as a non-crystalline combining matrix. This is in contrast to blends of POSS-SH and PHAE, where incompatibility occurred and the two components crystallized independently. The covalent links between PHAE and POSS imposed spatial constraint which resulted in disordered crystalline POSS domains and limited crystal sizes. With increasing POSS content, the appearance of these POSS-based biopolyesters changed from non-sticky and elastic to brittle and glass-like. The covalent linking of POSS-SH to PHAE increased the heat stability such as glass transitions, and melting points could be tailored between 48 and 120 °C.

Keywords: PHA; Poly[3-hydroxyalkanoate]; POSS

1. Introduction

In the field of inorganic–organic hybrid polymers, there is growing interest in polyhedral oligomeric silsesquioxane-based systems [1–5]. Silsesquioxanes with the general $RSiO_{1.5}$-stoichiometry include random structures, ladder structures, and cage or partial cage structures. Polyhedral oligomeric silsesquioxanes with specific cage structures have been designated by the abbreviation POSS [1]. The most representative members of this POSS family consist of Si_8O_{12} arranged in an inner eight-cornered cage, while the corners of this nanosized cluster are substituted with organic groups (R). Depending on the number of organic groups bearing reactive functionalities, POSS can be classified as non-functional, monofunctional, or polyfunctional.

POSS chemicals with reactive functionalities are suitable for polymerization, grafting or surface bonding. The incorporation of these nanoparticle reinforcing agents [6] into polymeric materials can lead to property improvements, such as temperature and oxidation resistance [7], surface hardening, and reduced flammability [8]. A variety of POSS-containing copolymers have been synthesized [1–5], and these hybrid materials have potential in areas such as stabilized semiconducting polymers in optoelectronic devices [9,10] or as low-dielectric-constant materials in the microelectronics industry [11].

Here, we report on the POSS-functionalization of poly[3-hydroxyalkanoates], PHAs, which are a family of high

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[*] Corresponding author. Address: Laboratory for Functional Polymers, Materials Science and Technology (Empa), Überlandstr. 129, CH-8600 Dübendorf, Switzerland. Tel.: +41 182 340 84; fax: +41 182 340 12.

E-mail address: roland.hany@empa.ch (R. Hany).

[1] Present address: Toyota Central Research & Development Laboratories, 41-1, Aza Yokomichi, Oaza Nagakute, Nagakute-cho, Aichi-gun, Aichi-ken 480-1192, Japan.

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doi:10.1016/j.polymer.2005.04.020

molecular weight polyesters synthesized by a wide variety of microorganisms [12]. The best-known PHA is poly[3-hydroxybutyrate], a highly crystalline biodegradable thermoplastic, also available as a random copolymer with valerate. On the other hand, medium-chain-length (mcl-) PHAs [13], which contain C6–C12 alkanoate monomers, are soft and/or sticky thermoplastic elastomers. mcl-PHAs can contain side chains with functional groups [12,14], which provide sites for further chemical modification, directed to modulate the basic polymer properties or to create functionalities which are impossible to introduce by biosynthesis [15].

Because they are biodegradable and biocompatible polyesters, PHAs are attractive for medical applications including release systems, implants and scaffolds in tissue engineering [16]. However, the lack of structural and functional stability prevents currently available PHAs from having wide-spread commercial impact. To take advantage of the property enhancements of polymers reinforced with nanofillers [5,6], we covalently attached a monofunctional POSS molecule containing seven isobutyl and one mercaptopropyl group, POSS-SH, via a free radical addition reaction to the side-chain alkenes of poly[3-hydroxyalkanoate-*co*-3-hydroxyalkenoate], PHAE, and report on the characterization of these novel POSS-based biopolyesters.

2. Experimental

2.1. Biosynthesis of poly[3-hydroxyalkanoate-co-3-hydroxyalkenoate], PHAE

PHAE was produced in a chemostat culture of *Pseudomonas putida* GPo1 (ATTC 29347) at a dilution rate of 0.1 h^{-1} under multiple (C, N) nutrient limited growth conditions [17]. Cells were fed with different mixtures of octanoate, 10-undecenoate, and a mineral medium. The medium was designed in such a way that only nitrogen and carbon limited growth, whereas all other nutrients were in excess. The ratio of the feeds of octanoate and 10-undecenoate was adjusted to control the fraction *m* of side-chain double bonds in PHAE-*m*. Thus, PHAE-11.5 with 11.5 mol% alkenes, as well as PHAE-55, PHAE-78, and PHAE-97 were produced.

2.2. Synthesis of PHAE-m-POSS

All reagents were purchased from Fluka or Aldrich. Mercaptopropyl-isobutyl-POSS (POSS-SH) was further purified by sublimation under vacuum (approximately 3 mbar) at 210–230 °C. POSS-SH is highly soluble in hexane, $CHCl_3$ or THF at room temperature, but only in boiling acetone. The solubility of POSS-SH in acetone at room temperature (4.4 g/L) was determined as follows: 250 mg POSS-SH in 25 mL acetone was stirred for 16 h. Ten milliliters of the suspension were then centrifuged, 5 mL of the solution collected in a weighed flask, the solvent evaporated and the flask dried at 10^{-6} bar. The amount of residue was determined by weight. For the synthesis of PHAE-11.5-POSS, 10 g of the starting polyester (8.2 mmol PHAE double bonds), 14.6 g of POSS-SH (16.4 mmol), and 269 mg of AIBN (1.64 mmol, 2,2′-azoisobutyronitrile) were dissolved in 100 mL toluene under argon. The solution was heated to 75 °C for 18 h, cooled to room temperature, dropped into 1 L of ice-cold methanol, and the precipitate (21.3 g of PHAE-11.5-POSS and POSS-SH) was then dried under high vacuum. POSS-SH was removed from PHAE-11.5-POSS by slowly stirring the raw product in acetone (1:10 w/v) at room temperature, the suspension was centrifuged, the supernatant collected, the solvent removed and PHAE-11.5-POSS was then dried under high vacuum. The synthesis of PHAE-*m*-POSS, with $m=55$, 78, and 97, was carried out as described above. However, in contrast to PHAE-11.5-POSS, these products were not soluble in acetone. Therefore, POSS-SH could be removed by repeated boiling in refluxing acetone and collecting the sediment after centrifugation.

2.3. Polymer characterization

Proton NMR experiments in solution were performed on a Bruker AV-400 spectrometer. The measurements were carried out at 300 K with typically 10 mg of sample dissolved in 0.7 mL solvent. Chemical shifts are given in ppm relative to the remaining signal of chloroform at 7.26 ppm. Cross polarization, magic angle spinning (CP/MAS) ^{13}C NMR spectra were recorded on a Chemagnetics CMX-300 instrument operating at 75.4 MHz. Samples were packed in 7.5 mm rotors and spun at 4 kHz. A contact time of 3 ms and a recycle delay of 3 s were used. Single pulse Bloch decay spectra were obtained using a 60° pulse and a recycle delay of 3 s. Molecular weights were determined by gel permeation chromatography (GPC, Viscotek, Houston, TX, USA) equipped with a RI detector. The system was calibrated by using 10 polystyrene standards with known M_w (2×10^3 to 2.13×10^6 g mol^{-1}) and low polydispersity ($M_w/M_n \leq 1.09$). Forty milligrams of every sample was dissolved in 10 mL THF overnight. Aliquots of 100 μL of the polymer solution were chromatographed at 35 °C with pure THF as solvent phase through 2 GPC-columns (Mixed-Bed, Viscotek, Houston, TX, USA) at a flow rate of 1 mL/min. X-ray diffraction data were recorded using a Bruker AXS D8 Discover instrument with a GADDS powder diffractometer and CCD camera detector. Cu Kα radiation was generated at 40 kV and 40 mA. Thermal gravimetric analysis was performed with 4–10 mg of sample from room temperature to 650 °C on a 2950 thermogravimetric analyzer from TA instruments. The gas flow (oxygen or nitrogen) was 20 mL/min, and the heating rate was 5 °C/min. To prevent the loss of the powdered POSS-SH (and decomposition products) in the gas stream, the aluminium pot was covered with a perforated top. Differential scanning calorimetry measurements in a nitrogen atmosphere were carried out on a Mettler Toledo Star^{e} DSC System. Nine to fifteen milligrams of sample were heated from room temperature to 200 °C, subsequently removed, and quenched in liquid nitrogen. DSC data were then recorded for the temperature program −80 to 200 °C, cooling to −80 °C, followed by heating to 350 °C, all at a rate of 10 °C/min.

3. Results and discussion

Different feed mixtures of octanoate and 10-undecenoate in a chemostat culture of *Pseudomonas putida* GPo1 were used for the biosynthesis of poly[3-hydroxyalkanoates-*co*-3-hydroxyalkenoates] with varying fractions *m* of side chains with terminal double bonds, PHAE-*m*. The conversion of the carbon sources by fatty acid degradation (β-oxidation) lead to the incorporation of shorter monomer units as well, and we adopted the experimentally [18] determined ratios 3-hydroxyhexanoate:3-hydroxyoctanoate = 1:6.5, and 3-hydroxyheptenoate:3-hydroxynonenoate:3-hydroxyundecenoate = 1:3.6:1, for all PHAE copolymers of this work. The reaction scheme for the free-radical addition of POSS-SH to the side-chain double bonds of PHAE is shown in Fig. 1. The reactions were carried out in toluene and AIBN was the radical initiator, as described recently for the similar transformations using 11-mercapto-1-undecanol [19] or 11-mercaptoundecanoic acid [18].

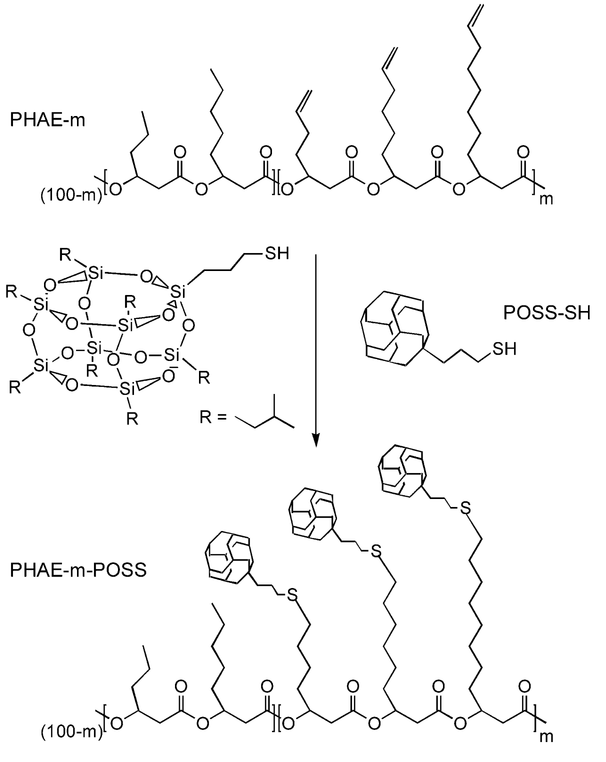

Fig. 1. Free radical addition reaction of mercaptopropyl-isobutyl-POSS (POSS-SH) to the side-chain double bonds of poly[3-hydroxyalkanoate-*co*-3-hydroxyalkenoate], PHAE.

Reaction conversions were obtained from ^{1}H NMR spectra. Fig. 2(a) shows the spectrum of POSS-SH with the assignment of the isobutyl and mercaptopropyl resonances. In the NMR spectra of the starting polyesters, as displayed in Fig. 2(b) for PHAE-11.5, the intensity of the methine backbone protons was set to 100 (mol%). The fraction of unsaturated side-chain double bonds (11.5%) was then directly obtained from the intensity of the alkene resonances at 5.77 ppm, and was cross-checked via the intensity of the three equivalent methyl protons of 3-hydroxyoctanoate and 3-hydroxyhexanoate at 0.88 ppm (266/3 = 88.7), representing the rest of 88.5 mol% of saturated monomer units. The remaining intensity of 1.1 for the alkene resonances in the NMR spectrum of PHAE-11.5-POSS shown in Fig. 2(c) points to a conversion of 10.4 mol% alkene groups during the reaction. From the POSS NMR resonances *b* (one proton) and *a* (two protons) of the seven isobutyl groups, a POSS content of 10.5 mol% can be calculated. The good agreement between the decrease of the olefinic resonances (conversion of 90.4% of all double bonds) and the appearance of POSS (suggesting the conversion of 91.2% of the alkenes into thioether groups) in the NMR spectrum of PHAE-11.5-POSS agrees with the smooth free-radical addition of thiols to PHAE observed recently [18,19] and excludes significant side reactions. We note, that due to the

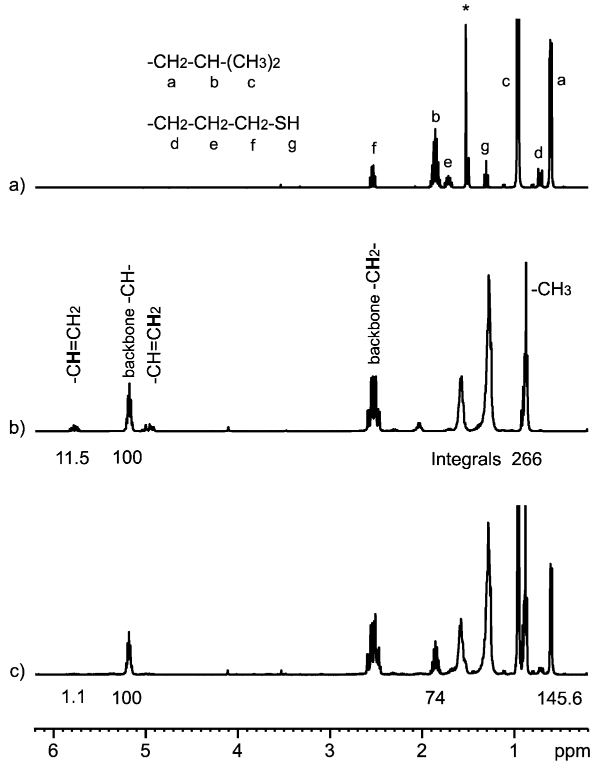

Fig. 2. ^{1}H NMR spectra of (a) POSS-SH, (b) PHAE-11.5, and (c), PHAE-11.5-POSS. The chemical structures are shown in Fig. 1. The numbers under certain resonances are relative intensity values and residual solvent signal is marked with * at 1.50 ppm in (a).

purification process and the limited solubility of POSS-SH at room temperature (see Section 2), PHAE-11.5-POSS was still contaminated with approximately 4 wt% of unreacted POSS-SH. The other PHAE-*m*-POSS samples could be cleaned completely from excess POSS-SH. Also for these reactions, the degree of conversion of double bonds as determined from the decrease of alkene resonances or the appearance of POSS agreed within 8%. The results and the weight percent of POSS in the PHAE-*m*-POSS copolymers are summarized in Table 1.

Molecular weights were measured to monitor the polymer-analogous reactions (Table 1). M_n values of typically 100,000 g/mol and $M_w/M_n=2$ were found for the starting polyesters [20], and the molecular weights increased for the PHAE-*m*-POSS reaction products. M_n values were also calculated for PHAE-*m*-POSS, based on the known starting copolymer compositions, the experimental M_n values for PHAE-*m* and the reaction conversions. These calculated molecular weights were considerably higher than the experimental results, and decreasing ratios $M_{n,exp}/M_{n,calc}$ from 0.6 to 0.39 with increasing POSS content were obtained (Table 1). The same was true for POSS-SH alone, where $M_{n,exp}/M_{n,calc}$ was 0.63. Therefore, these differences must be explained with differences in terms of the hydrodynamic volumes of the products in THF due to the presence of POSS in the side chains, and are not indicative of considerable side reactions with by-products not detectable by ^{1}H NMR spectroscopy. Low molecular weight data of POSS copolymers based on GPC with polystyrene calibration have been mentioned in the literature recently [21].

Considering the size of the POSS molecule with a diameter of approximately 1.5 nm, the high conversion yields are surprising. For PHAE-97-POSS, the conversion of 74.5% of double bonds means that 72% of all PHAE side chains had covalently linked to a bulky POSS molecule. It must be noted that the reactions were not optimized for high conversions, since we added, for economic reasons, only a two molar excess of POSS-SH, instead of the four molar excess of thiols we used for the quantitative transformations of PHAE alkene groups earlier [18,19]. Qualitatively, the incorporation of POSS had a strong influence on the appearance of thin films cast from chloroform solutions on microscope slides. Films of PHAE-11.5 could be removed and were highly elastic, whereas PHAE-97 was a material of honey-like consistency too sticky to be peeled off from the glass surface. For the POSS copolymers, the trend was reversed: PHAE-11.5-POSS appeared as a non-sticky, but still elastic film material, and PHAE-97-POSS formed a highly transparent and very brittle, glass-like film. Finally, for blends of PHAE-11.5 or PHAE-97 with POSS-SH, demixing was observed and the material looked like POSS powder stuck together with PHAE. Apparently, the POSS isobutyl side groups are not compatible with the polymer matrix. The covalent attachment of POSS-SH to PHAE imposed spatial constraint and hindered the phase separation process of the copolymers [5].

The X-ray powder pattern of POSS-SH (Fig. 3) showed four main diffraction peaks at 8.3, 11.1, 12.1 and 19.3° (2Θ) in the diffraction diagram which correspond to 1.07, 0.80, 0.73 and 0.46 nm, respectively. These values are typical for POSS [22,23]. Five diffraction peaks at 4.9, 11.7, 18.3, 19.5 and 21.3° (2Θ) were observed in the X-ray powder diffractogram of PHAE-11.5, which clearly differed from the values obtained for POSS-SH. The *d* spacing value at 4.9° corresponds to 1.8 nm and is a characteristic of crystalline medium-chain-length PHA, such as poly(3-hydroxyoctanoate) [24]. This observation is reasonable because PHAE-11.5 contains 88.5% of 3-hydroxyhexanoate and 3-hydroxyoctanoate monomer units as well. PHAE-11.5-POSS did not have the diffraction peaks derived from PHAE, especially the characteristic diffraction at 4.9° (2Θ) was missing, but it showed all the typical diffractions of POSS in the X-ray pattern, suggesting that independent crystallization of POSS was favoured over that of PHAE-11.5. A blend of PHAE-11.5 and POSS-SH

Table 1
Compositions and characteristics of poly[3-hydroxyalkanoates-*co*-3-hydroxyalkenoates], PHAE-*m*, and PHAE-*m*-POSS derivatives

Sample	Conversion of PHAE double bonds (%)[a]	POSS in copolymers (wt%)	$M_{n,exp}$[b]	$M_{w,exp}/M_{n,exp}$	$M_{n,exp}/M_{n,calc}$	T_g (°C)	T_m (°C)
POSS-SH			0.56	1.1	0.63		257[c]
PHAE-11.5			106	2.1		−36	53
PHAE-55			90	2.2		−44	41
PHAE-78			94	2.1		−47	
PHAE-97			107	2.2		−48	
PHAE-11.5-POSS	91.2	40.1	107	4.5	0.60	−35	48
PHAE-55-POSS	72.7	70.8	161	2.6	0.52	−34	90
PHAE-78-POSS	67.9	75.8	177	2.4	0.44	−38	105
PHAE-97-POSS	74.5	80.8	215	4.2	0.39	−36	120

m denotes the fraction (%) of side-chain double bonds in PHAE, see Fig. 1.
[a] From ^{1}H NMR data.
[b] ($\times 10^3$ g/mol).
[c] An additional small endotherm was measured at 23.5 °C, see Fig. 6.

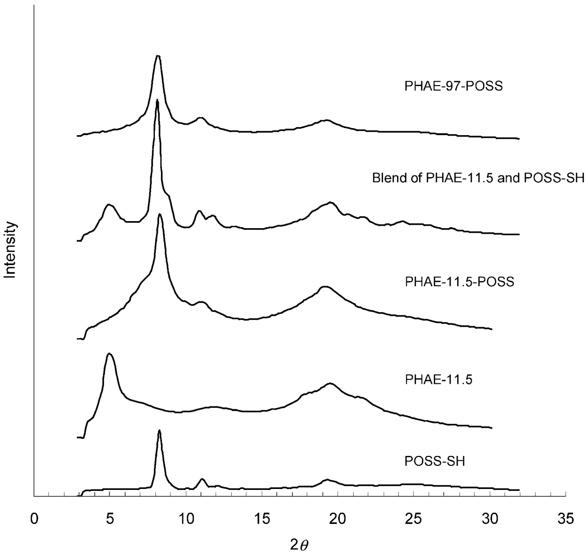

Fig. 3. X-ray powder diffraction diagrams for POSS-SH, PHAE-11.5, and PHAE-*m*-POSS derivatives.

displayed an X-ray pattern as the superposition of both components and the diffractions from PHAE-11.5 were evident. The X-ray powder pattern of PHAE-97-POSS was similar to that for PHAE-11.5-POSS, meaning that the crystalline component of PHAE-97-POSS was only POSS in this case, too. The POSS diffraction at 8.3° is of broader width for both PHAE–POSS derivatives shown in Fig. 3, which points to disordered crystalline domains and limited crystallite sizes.

The model for crystalline medium-chain-length PHA reported previously [25] consists of two principal spacings in a sheet-like structure: one spacing corresponding to 1.8 nm is due to the periodicity between helical main chains with twofold symmetry in the sheets [24], the other is interplanar spacing with 0.46 nm between the sheets. This organization was disrupted when POSS-SH was covalently attached to PHAE, and PHAE-11.5-POSS did not show a 1.8 nm maximum indicating that PHAE became a non-crystalline matrix for the crystalline POSS. The same was true for PHAE-97-POSS. When a blend was examined, the crystalline structures of both POSS-SH and PHAE were maintained, which supports the qualitative observation of demixing and phase separation for cast films described above.

Solid-state ^{13}C NMR spectra of PHAE-11.5-POSS are shown in Fig. 4. The single-pulse Bloch decay MAS experiment was used to detect both the mobile and more amorphous, as well as the more crystalline and thus rigid components. In Fig. 4(a), POSS resonances are visible at 24, 25 and 29 ppm. For the PHAE component, the resonances for the backbone carbonyl carbons, –CH– and –CH$_2$– groups, appear at 172, 72 and 39 ppm, and for the side-chain –CH$_2$– and –CH$_3$ groups they appear at 24, 25, 31, 34, and 15 ppm [24,26]. As expected, no resonances are visible from the PHAE alkene groups at 115 and 139 ppm, which proves that most double bonds have reacted with POSS-SH. Compared to pure PHAE-11.5 (data not shown), the NMR signals of the backbone carbons are broadened in Fig. 4(a), implying that PHAE was in a more disordered environment after reaction with POSS-SH. The cross-polarization (CP) spectra of PHAE-11.5-POSS in Fig. 4(b) shows mainly POSS resonances, suggesting that the PHAE component was mobile and non-crystalline. This is in keeping with the X-ray results displayed in Fig. 3. Also for a blend of PHAE-11.5 and POSS-SH, the CP spectrum was equivalent to the superposition of both individual components, confirming that the crystallization of POSS only was favoured in the derivatives. The spectrum of PHAE-97-POSS was similar to that of PHAE-11.5-POSS, and, because of the high weight fraction and dominant signal intensities of POSS in the PHAE-97-POSS sample, no relevant differences were detectable between the single-pulse and CP NMR spectra.

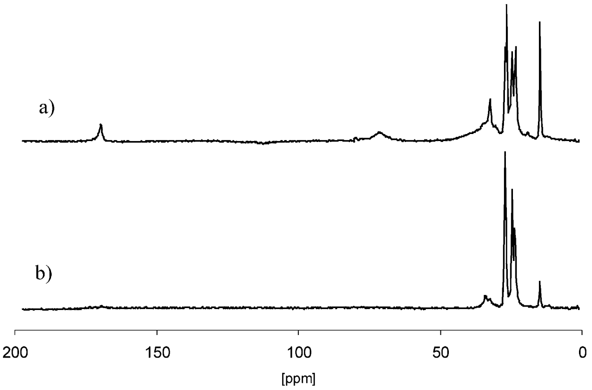

Fig. 4. Single pulse Bloch decay MAS (a) and CP/MAS (b) ^{13}C NMR spectra of PHAE-11.5-POSS.

Selected thermal gravimetric traces are shown in Fig. 5. The weight loss of PHAE-11.5 in an oxygen atmosphere started at approximately 270 °C, and the weight loss at 300 °C was greater than 80%. PHAE-11.5 decomposed almost completely for temperatures greater than 500 °C. In nitrogen, the decomposition behaviour was similar, and the gravimetric trace was shifted to lower temperatures by approximately 10 °C. All PHAE samples decomposed identically. The decomposition of POSS-SH in oxygen started at 300 °C, the 20% weight loss occurred at 340 °C, and the weight residue was 52.8% at 650 °C. This can be explained by the oxidative decomposition of POSS into SiO$_2$, since the calculated weight residue for this transformation is 53.9%, close to the experimental value. When POSS-SH was heated under nitrogen, the weight loss started at 290 °C, the 90% weight loss occurred at 400 °C, and no residue remained above 600 °C. This points to a complete transformation into volatile products or sublimation of POSS-SH in a nitrogen atmosphere. A steady increase of the thermal stability with increasing POSS amounts was observed for the PHAE–POSS derivatives in oxygen, and the 20% weight loss increased from 290 °C for PHAE-11.5-POSS to 320 °C for PHAE-97-POSS. Again,

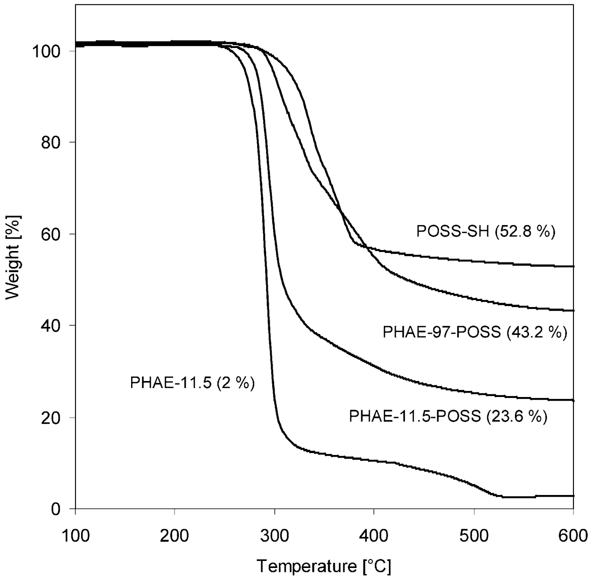

Fig. 5. Thermal gravimetric traces in O_2 atmosphere of POSS-SH, PHAE with 11.5 mol% side-chain double bonds, and selected PHAE–POSS derivatives. The numbers in brackets denote the experimental weight residues at 650 °C.

the weight residues at 650 °C can be explained with remaining SiO_2. This was confirmed by comparison with the calculated SiO_2 residues from the known weight fractions of POSS in PHAE-*m*-POSS (Table 1). These values are 21.6% for PHAE-11.5-POSS and 44.2% for PHAE-97-POSS, close to the experimental weight residues shown in Fig. 5.

Fig. 6 shows DSC traces for selected samples. The melting endotherm, T_m, of POSS-SH is at 257 °C (Table 1), which is close to the TGA weight loss onset temperature of approximately 290 °C. A further small endotherm of unknown origin is visible at 23.5 °C. In preliminary measurements we observed a similar solid-state transformation at 50 °C for the structurally related chloropropyl-isobutyl-POSS molecule ($T_m = 265$ °C). Melting points at 53 and 41 °C were observed for PHAE-11.5 and PHAE-55, whereas PHAE with higher contents of unsaturated side groups are known to be amorphous [20]. The POSS content in the copolymers had a drastic effect on the melting points. For PHAE-11.5-POSS, T_m was 48 °C, slightly lower than T_m of PHAE-11.5, but increased up to 120 °C for PHAE-97-POSS. As shown by XRD diffraction, these melting endotherms are due to the crystalline phase of POSS, and the lower melting points suggest small and imperfect crystals. It is interesting to note that T_m of PHAE-97-POSS is considerably higher than the highest melting point achieved for PHA variants obtained by incorporation of modified fatty acids. There, a maximum $T_m = 100$ °C has been obtained for a PHA containing fluorinated phenoxy side groups [27]. The glass transition temperatures for the PHAE–POSS copolymers varied only slightly between $T_g = -34$ and -38 °C. A comparison of the starting polyesters with their products shows that T_g remained constant for PHAE-11.5-POSS, and increased by approximately 10 °C for the other POSS derivatives. This has been observed in many other copolymers when sufficient POSS was incorporated, and has been explained by the POSS–POSS and POSS–PHAE interactions, resulting in retarded polymer chain mobility and T_g enhancement [1]. However, an initial T_g decrease at low POSS contents due to the inert diluent role of POSS was not observed here [28].

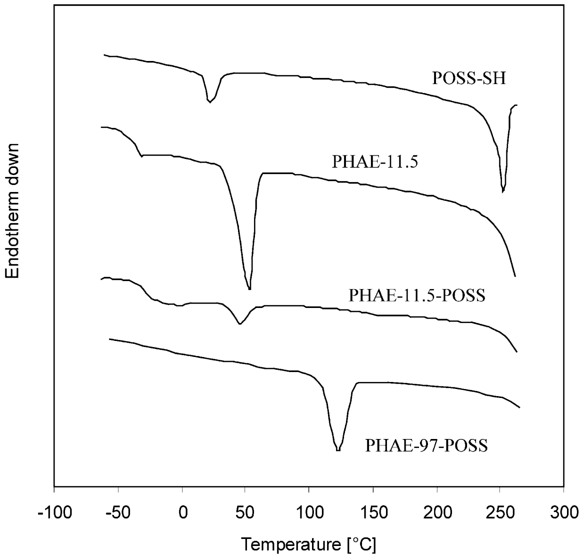

Fig. 6. DSC traces of POSS-SH, PHAE-11.5, and PHAE-*m*-POSS derivatives. The presented traces were taken after slowly cooling down the samples to −80 °C. For PHAE-97-POSS, the glass transition was observable only after quenching in liquid nitrogen (see Table 1).

4. Conclusion

The POSS-based biopolyesters of this work form a new family of organic–inorganic hybrid materials. The incorporation of POSS significantly changed the physical properties of mcl-PHAs and could eliminate their notorious stickiness. These findings agree well with the results of our previous study on the functionalization of mcl-PHA double bonds with long polyethylene-like chains [18]. Clearly, the potential application of these POSS-based biopolyesters has yet to be demonstrated. Recent results indicate that such systems might well be classified as non-toxic and suitable for food contact and not harmful if swallowed [29,30].

Acknowledgements

We thank E. Pletscher for his effort in the fermentation process, and M. Schmid and A. Hinz for their help with DSC and GPC analyses. F. Morin at McGill University was responsible for the solid-state NMR spectra.

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