Characterization of bi-layered magnetic nanoparticles synthesized via two-step surface-initiated ring-opening polymerization

Abstract: A versatile strategy to integrate multiple functions in a polymer based material is the formation of polymer networks with defined nanostructures. Here, we present synthesis and comprehensive characterization of covalently surface functionalized magnetic nanoparticles (MNPs) comprising a bi-layer oligomeric shell, using Sn(Oct)$_2$ as catalyst for a two-step functionalization. These hydroxy-terminated precursors for degradable magneto- and thermo-sensitive polymer networks were prepared via two subsequent surface-initiated ring-opening polymerizations (ROPs) with $\omega$-pentadecalactone and $\varepsilon$-caprolactone. A two-step mass loss obtained in thermogravimetric analysis and two distinct melting transitions around 50 and 85 °C observed in differential scanning calorimetry experiments, which are attributed to the melting of OPDL and OCL crystallites, confirmed a successful preparation of the modified MNPs. The oligomeric coating of the nanoparticles could be visualized by transmission electron microscopy. The investigation of degrafted oligomeric coatings by gel permeation chromatography and $^1$H-NMR spectroscopy showed an increase in number average molecular weight as well as the presence of signals related to both of oligo($\omega$-pentadecalactone) (OPDL) and oligo($\varepsilon$-caprolactone) (OCL) after the second ROP. A more detailed analysis of the NMR results revealed that only a few $\omega$-pentadecalactone repeating units are present in the degrafted oligomeric bi-layers, whereby a considerable degree of transesterification could be observed when OPDL was polymerized in the 2nd ROP step. These findings are supported by a low degree of crystallinity for OPDL in the degrafted oligomeric bi-layers obtained in wide angle X-ray scattering experiments. Based on these findings it can be concluded that Sn(Oct)$_2$ was suitable as catalyst for the preparation of nanosized bi-layered coated MNP precursors by a two-step ROP.

Keywords: degradable polyester; magnetic nanoparticles; nanoparticle characterization; NICE-2014; ring opening polymerization; surface functionalization.

Introduction

Magneto responsive nanomaterials are of great scientific and technological interest in recent years [1–3] and their unique functionalities are widely used in biomedical and pharmaceutical applications [4–10]. Iron oxide
based colloids such as magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃) have been reported to be functionalized and applied as contrast agents for tumor imaging [11, 12], cancer therapy including hyperthermia approaches as well as cell labeling agents [13, 14]. To achieve well defined nanostructured magneto-responsive materials, different desired functionalities of magnetic nanoparticles (MNPs) can be generated either by physical or covalent modifications of the particle surface with polymers or low molecular weight bioactive compounds, thus receiving well defined MNP functionalized precursors. Physical modification enables the encapsulation of magnetic nanoparticles in polymeric shells by mixing or in-situ precipitation [15–17]. Chemical modification can be obtained by either ‘grafting to’ or ‘grafting from’ approaches. A recent example for the ‘grafting to’ method is click chemistry which is highly efficient [7, 18–20]. The characterization of hybrid-nanomaterials such as oligomer functionalized MNPs represents a major challenge, as here both the inorganic core as well as the organic shell have to be explored using various analytical techniques [1, 7, 21, 22]. Surface-initiated polymerization is a powerful method which can be applied onto MNPs surfaces as a ‘grafting-from’ method, resulting in an ideal molecular structure. More specifically, the polymerization is initiated directly from functional groups e.g. hydroxyl groups at the particle surface. For example, lactones, such as rac-dilactide, ε-caprolactone, ω-pentadecalactone or epoxides have been reported as candidates for the surface initiated ring-opening polymerization (ROP) [23–27]. In this context catalysts like Sn(Oct), have been applied for ROP of lactones [28, 29] under mild reaction conditions. Besides the modification with one type of hydrophobic or hydrophilic polymer, recently magnetite nanoparticles comprising both a hydrophobic inner shell and a hydrophilic outer shell have been described [30, 31]. One report describes the synthesis of amphiphilic block copolymers consisting of a hydrophilic methoxy poly(ethylene glycol) block and a hydrophobic polyester block which were ‘grafted onto’ a magnetite nanoparticle surface [31]. Another approach started by coating the magnetite particles with oleic acid, attaching at first a polyvinylbenzyl chloride layer by miniemulsion polymerization and in a second step a poly(ethylene glycol) hydrophilic layer by condensation reaction [30].

Magneto-sensitive materials can be obtained by incorporation of MNPs as active fillers into thermo-sensitive polymers, responding resonantly to an alternating magnetic field and in such a way enabling magnetic targeting as well as non-contact heating, which can be applied for activation of shape-memory effects [32–35]. The preparation of magneto-sensitive macroscopic composite materials, where the functionalized nanofillers are physically embedded into a macroscopic polymer matrix [26] or microparticles [34, 36] have been reported. It could be demonstrated that oligo(ε-caprolactone) coated MNPs can significantly improve the dispersion of MNPs in poly(ε-caprolactone) networks as well as the magnetic heating capability of the composite [26].

For the synthesis of polymer-based materials with desired architectures defined precursors are required. One example are polymer networks, which are synthesized via condensation of linear or star-shaped hydroxyl terminated oligomeric precursors and diisocyanates [37, 38]. This concept has been applied for the controlled synthesis of hybrid-nanomaterials in which polymer grafted magnetite nanoparticles are used as precursors of hybrid polymer networks where the nanoparticles act as multi-functional netpoints [27, 36, 38].

Here, we explored whether modified MNPs comprising a covalently attached two-layer coating of oligo(ω-pentadecalactone) (OPDL) and oligo(ε-caprolactone) (OCL) can be achieved by a two-step surface-initiated ring-opening polymerization (ROP) of the related lactones, in order to gain well-defined precursors for polymer networks with defined nanostructure, by using Sn(Oct), as a coordination-insertion catalyst. After polymerization of a first polymeric layer onto the MNPs a second ROP is catalyzed by the remaining Sn(Oct), moieties from the first ROP. In this way, two types of bi-layered coated MNPs were prepared one with OCL as inner polymeric layer and OPDL as outer surface layer named MNP-OCL-OPDL and a second one with the reversed sequence of the oligomeric layers (MNP-OPDL-OCL). The composition of the achieved hybrid nanomaterials was studied by thermogravimetric analysis (TGA). Transition electron microscopy (TEM) was utilized to determine the nanoparticles’ size and the thickness of the oligomeric coatings. The degrafted oligomeric coatings were analyzed by gel permeation chromatography (GPC) and proton nuclear magnetic resonance (¹H-NMR) spectroscopy. Infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and wide angle X-ray scattering (WAXS) were applied for elucidation of the two-layer structure.
Experimental

Materials

Ferric chloride hexa-hydrate (≥97%, FeCl₃·6H₂O), ferrous chloride tetra-hydrate (98%, FeCl₂·4H₂O), ammonium hydroxide solution (28–30% NH₄OH in H₂O), glycolic acid, ε-caprolactone (97%), ω-pentadecalactone (PDL), chloroform (≥99%), tin(II) 2-ethylhexanoate (95%, Sn(Oct)₂), and hydrochloric acid were of analytical grade and were obtained from Sigma-Aldrich (Munich, Germany). All the chemicals were used as received.

Synthesis of MNPs

Magnetite based MNPs were synthesized by a co-precipitation method from aqueous ferric and ferrous solutions at a pH > 7, according to [26]. Briefly, 10.8 g of FeCl₃·6H₂O, 4.8 g FeCl₂·4H₂O and 10 mL NH₄OH were all dissolved in 100 mL deionized water with constant magnetic stirring for 12 h at room temperature. After additional 12 h deionized water was added to the precipitate and the supernatant was removed after centrifugation at 4000 rpm. This washing procedure with deionized water and centrifugation was conducted for 3 times. The pellet was dried in a vacuum oven at 50 °C for 12 h for obtaining the MNPs.

Surface modification of MNPs with a single oligomeric layer via ROP

Initial surface modification of MNPs with hydroxyl groups using glycolic acid was performed according to a procedure described in [26]. More specifically, 5.0 g pure MNPs were suspended in 45 mL deionized water, and 0.5 g glycolic acid was added to the aqueous suspension to functionalize the surface of the MNPs with hydroxyl groups, followed by a treatment with ultrasonication for 30 min. The reaction mixture was kept at ambient temperature for 12 h. Subsequently, the particles were washed repeatedly using 1.3% v/v aqueous NH₄OH solution to remove unreacted glycolic acid. Finally, the glycolic acid modified MNPs (named MNP-GA) were collected and dried in a vacuum oven at 60 °C for 12 h.

For covalent coating with oligo(ε-caprolactone) (OCL), 1 g MNP-GA, 2 g ε-caprolactone and 0.05 g Sn(Oct)₂ were reacted at 130 °C for 5 h under continuous stirring using nitrogen as protection gas according to the method described in [26]. Afterwards, the reaction mixture was cooled to ambient temperature, 10 mL chloroform were added, and the solution was centrifuged at 1500 rpm for 5 min. After centrifugation the sediment fraction containing unreacted MNPs was removed and the supernatant was collected and precipitated in hexane. The precipitated product was filtered by filtration funnel and dried at ambient temperature without applying vacuum, and the dried product was collected. Five gram dried product were redissolved in 10 mL chloroform in a 25 mL beaker and a permanent magnet was applied from the outside at the bottom side of the beaker for 30 min, the sediment fluid was collected and the rest of pellet was removed. The collected sediment fluid, containing oligomer coated MNPs, was poured into hexane for precipitation of the modified nanoparticles. The precipitated MNP product was filtered by filtration funnel and dried at ambient temperature in a vacuum oven at 3 mbar for 12 h, and the final product is named MNP-OCL.

For preparation of oligo(ω-pentadecalactone) (OPDL) modified MNPs a similar synthesis procedure according to the method described in literature [24] was applied, whereby 1 g MNP-GA, 5 g ω-pentadecalactone and 0.05 g Sn(Oct)₂, were reacted at 130 °C for 21 days using nitrogen as protection gas under continuous stirring. The reaction mixture was then cooled to ambient temperature and 10 mL chloroform were added. After applying the identical purification procedure as described for MNP-OCL, MNP-OPDL was obtained.
Synthesis of bi-layered modified MNPs

The hydroxyl end groups of the covalently attached oligomers in MNP-OCL and MNP-OPDL were used as initiator to synthesize bi-layered MNPs. For the second covalent coating with OPDL, 5 g MNP-OCL with Sn(Oct)₂ activated end-groups and 5 g ω-pentadecalactone were reacted at 130 °C for 21 days under continuous mechanical stirring using nitrogen as protection gas. The reaction mixture was afterwards cooled to 25 °C and 10 mL chloroform were added. The solution was centrifuged at 1500 rpm for 5 min. The supernatant was treated following the same procedure above and the final product was named MNP-OCL-OPDL.

By applying the identical synthetic method and purification procedure as described for MNP-OCL-OPDL, MNP-OPDL-OCL was obtained.

Degrafting of oligomeric shells from the modified MNPs

Degrafting of the oligomeric shells was proceeded by adding 20 mL 1 M aqueous HCl to 100 mg of modified MNPs, which have been dispersed in 10 mL chloroform according to the method described in literature [24, 26]. The mixture was stirred at room temperature until a yellow color was achieved. Next the magnetite nanoparticles were separated with the help of a permanent magnet from the organic phase. After drying the organic phase with anhydrous MgSO₄ for 12 h the degrafted oligomers were precipitated in hexane and dried in vacuo until constant weight was achieved before further analysis was performed.

Characterization techniques

TGA experiments were performed on a Netzsch TGA 204 Phoenix (Netzsch, Selb, Germany). All experiments were conducted with a constant heating rate of 10 K·min⁻¹. The samples were heated from 25 to 600 °C under N₂ atmosphere.

Transition electron microscopy (TEM) investigations were performed on a Talos F200A (FEI, Eindhoven, The Netherlands) with high-brightness electron source (X-FEG) and an information limit of 0.12 nm. The prepared samples were all analyzed at 200 kV using a CompuStage Single-Tilt holder (FEI, Eindhoven, The Netherlands). The images were obtained with a CMOS technology based camera model Ceta 16M (FEI, Eindhoven, The Netherlands) with 4000×4000 pixels. For sample preparation a small amount of nanoparticles were dissolved in 2 mL chloroform and placed for 10 min in an ultrasonic bath at ambient temperature. The samples were allowed to settle overnight. A Lacey-carbon film on 400 mesh copper grid with 42 μm mesh size was dipped into the supernatant and the residual chloroform was removed by a filter paper and finally the samples were dried by evaporation at ambient temperature. The mean diameter of the magnetite nanoparticle cores was determined by analyzing the particle area of 190 particles. The average thickness of the polymeric shell was specified by measuring the coating thickness at three different places of the coating of five single particles for each modified MNP utilizing the Scandium Software version 5.2 (Olympus Soft Imaging Solutions GmbH).

FTIR spectra were obtained by the attenuated total reflection (ATR) technique using a Magna-IR 550 infrared spectrometer (Nicolet Instruments GmbH, Neu-Isenburg, Germany) mounted with a MTC/B detector of 0.4 cm⁻¹ resolution.

The degrafted oligomeric polyesters were analyzed regarding their number average molecular weight \( \bar{M}_n \) by gel permeation chromatography (GPC). Multidetector GPC measurements were performed using 50 mmol ammonium acetate in N,N-dimethylformamide at 35 °C as eluent with a flow rate of 0.25 mL·min⁻¹ and 0.005 wt% BHT (2,6-di-tert-butyl-4-methylphenol) as internal standard. The system was equipped with 250 mm × 4.6 mm GRAM (polyester copolymer) gel columns, 3 × 10⁻¹ nm porosity, 10 μm particle size (Polymer Standard-Service GmbH, Mainz, Germany, PSS), a degasser (ERC-3315, Riemerling, Germany), a gradient pump PU 980 and an automatic injector AS-851 (both Jasco, Tokyo, Japan). Three detectors were used: a multi
wavelength detector MD-910 (270 nm), a RI-930 (both Jasco) and the viscosimeter n-1001 (WGE, Dr. Bures, Dallgow, Germany), which were combined by a split. For measurement and evaluation, the software Borwin-PDA 1.5 (Jasco) and WINGPC 6.2 (PSS) were used. All molecular weights were determined using a universal calibration with polystyrene standards (PSS).

The degrafted oligomeric polyesters were further analyzed by proton and carbon nuclear magnetic resonance (1H-NMR, 13C-NMR) spectra, recorded on a 500 MHz Avance spectrometer (Bruker, Karlsruhe, Germany) in deuterated chloroform with tetramethylsilane (TMS) as internal standard. By comparing the ratio between the integral of peak g (I_g) to the integral of peak c (I_c) and peak f (I_f), the number of repeating units (n) can be calculated as shown in eqs. (1) and (2). Number average molecular weights (\(M_n\)) were calculated according to eq. (3), in which the molecular weight for \(\varepsilon\)-caprolactone (CL) is \(M_{\text{CL}} = 114 \text{ g·mol}^{-1}\), while \(M_{\text{PDL}} = 240 \text{ g·mol}^{-1}\) for \(\omega\)-pentadecalactone (PDL).

\[
\begin{align*}
n_{\text{CL}} &= \frac{I_c}{I_g} \\
n_{\text{PDL}} &= \frac{I_f}{8 I_g} \\
M_n &= n_{\text{CL}} \cdot M_{\text{CL}} + n_{\text{PDL}} \cdot M_{\text{PDL}}
\end{align*}
\]

Wide angle X-ray scattering (WAXS) measurements were conducted at ambient temperature utilizing a X-ray diffraction system Brucker D8 Discover (Bruker, Karlsruhe, Germany) with a two dimensional detector from Bruker AXS (Bruker, Karlsruhe, Germany) in transmission geometry. The relation of the peak position and full width at half maximum (FWHM) with the crystal size (l_c) is given by the Sherrer eq. (4),

\[
l_c = \frac{k \cdot \lambda}{B \cdot \cos \theta}
\]

where \(B\) = FWHM (in radians), \(\theta\) = half scattering angle, \(\lambda\) = wavelength of X-rays. \(l\), was determined from the main diffraction peak around \(2\theta = 21.5^\circ\), which can be attributed to the 110 planes of the orthorhombic crystal structure of PCL [26] as well as PPDL [24].

DSC measurements were carried out on a Netzsch DSC 204 (Netzsch, Selb, Germany) with a constant heating and cooling rate of 10 K·min^{-1}. The temperature ranges for the 1st and 2nd heating runs were from 25 to 150 °C and -100 to 150 °C, respectively. Data from the 2nd heating run were analyzed. The crystallinity index \((X_c)\) was calculated from the obtained melting enthalpies \(\Delta H_m\) according to eq. (5) with \(\Delta H_m^{\text{PCL}} = 134.9 \text{ J·g}^{-1}\) [39] for 100 % crystalline PCL and \(\Delta H_m^{\text{PPDL}} = 127 \text{ J·g}^{-1}\) [40] for 100 % crystalline PPDL.

\[
X_c = \frac{\Delta H_m}{\Delta H_m^{100\%}} \times 100\% 
\]

**Results and discussion**

As starting material for the hybrid nanomaterials magnetite nanoparticles have been prepared by a co-precipitation method from ferric and ferrous salt in an aqueous environment. TEM investigations revealed an average size of 12 ± 3 nm for the magnetite nanoparticles having an almost round shape. The synthesis pathway for preparation of bi-layer coated MNPs is shown in Scheme 1. First MNP-GAs having hydroxyl groups at the particles surfaces were obtained by modification of the MNPs using glycolic acid. Then, the MNP-GAs were used to initiate the ROP of CL or PDL, allowing the formation of the respective oligomeric coatings, with
Sn(Oct), as catalyst. Since both, MNP-OCL and MNP-OPDL, also contained hydroxyl groups as end groups, with the existence of Sn(Oct), activated end groups of the molecules they can be further used to initiate the ROP of OPDL and OCL again. It is anticipated that during treatment of the grafted oligomers by reaction with 1N HCL the Sn-catalyst will be completely removed as demonstrated by Yoon et al. for a poly(p-dioxanone) grafted gold surface by X-ray photoelectron spectroscopy (XPS) investigation [28]. As shown in the Scheme 1a and b OCL was grafted from the previously generated MNP-OPDL, generating the bi-layered MNP-OCL-OPDL.

TGA experiments were conducted to explore the composition of the achieved products. As shown in Fig. 1, pure MNP has a slight mass loss of 3 wt% below 150 °C, possibly related to the evaporation of absorbed water inside the magnetite crystals. MNP-GA performed a mass reduction around 9 wt% between 200 and 300 °C, which can be attributed to the decomposition of surface attached glycolic acid. The single layer modified MNPs exhibited a similar mass loss of 39 wt% (MNP-OCL) and 38 wt% for MNP-OPDL, whereby the mass loss versus temperature curves of the OCL coated nanoparticles are shifted to higher temperatures. Determined from differentiated TGA curves (not shown here), the corresponding decomposition temperatures of OCL and OPDL in single layer MNPs were around 340–360 and 440–460 °C, respectively. These obtained results are in good accordance to the previously reported results in [24, 26].

The bi-layered nanoparticles MNP-OCL-OPDL and MNP-OPDL-OCL exhibited an overall mass loss of about 90 wt%, while showing almost identical two-step mass loss versus temperature curves indicating a successful second polymerization step. A more detailed analysis of the TGA curves revealed that almost 60 wt% of the mass loss can be attributed to the OCL decomposition, while 30 wt% belong to the decomposition of

\[ \text{Fig. 1: TGA curves of MNP (solid black line), MNP-GA (dashed black line) and MNP-OCL (solid light gray line), MNP-OCL-OPDL (dashed light gray line), MNP-OPDL (solid gray line) and MNP-OPDL-OCL (dotted gray line).} \]
OPDL. Compared to the mass loss of MNP-OCL and MNP-OPDL a significant decomposition was observed at lower temperatures around 300 °C. The decomposition temperatures of OCL and OPDL in MNP-OCL-OPDL were 358 and 395 °C, respectively, while in MNP-OPDL-OCL were 350 and 387 °C. The decomposition temperature of OCL in single layer MNPs (around 350 °C) was similar to that in bi-layered MNPs (358 and 350 °C). However, the decomposition temperature of OPDL in bi-layered MNPs (395 and 387 °C) was lower than that in single MNPs (around 450 °C).

Representative TEM micrographs of MNP with one and two oligomeric layers are shown in Fig. 2. For OCL coated MNPs an average layer thickness of 1.7 ± 0.2 nm was found, while a similar thickness around 1.8 ± 0.3 nm was obtained for MNP-OPDL (indicated by the white arrows in Fig. 2). Surprisingly the TEM analysis of the bi-layer functionalized nanoparticles revealed a lower thickness of the bi-layer polymeric coating of 1.4 ± 0.3 nm for MNP-OCL-OPDL and 1.3 ± 0.2 nm for MNP-OPDL-OCL when compared to the thickness of the single-layer functionalized MNPs. Besides the nanoparticulate aggregates shown in Fig. 2 large areas of the TEM samples were found to be solely coated with organic material, which is not the Lacey-carbon film or a deposition of evaporated contaminants (data not shown). This solely organic material might be attributed to oligomeric OCL and OPDL chains which are also formed during ROP and were not completely removed by the applied MNP purification.

Based on the obtained TGA results, where a mass loss of almost 90 wt% could be related to the mass of the oligomeric bi-layer, a theoretical thickness of the polymeric shell can be estimated. Here, we assume a spherical iron oxide core with a diameter of 12 nm (corresponding to the TEM results) having a density of 5.3 g·cm⁻³, while for the polymeric spherical shell a density of 1.0 g·cm⁻³ was presumed. In this way, an estimated polymeric shell thickness of about 22 nm was calculated. The large discrepancy of the calculated thicknesses of the modified MNPs and the results achieved from TEM analysis can be explained by the presence of a substantial amount of physically adsorbed or single OCL or OPDL oligomers in the purified MNPs (for details see Experimental).

In this context we exposed already purified MNP-OCL to a second purification step utilizing a much lower particle concentration of 5 g MNP dissolved in 500 mL chloroform. For separation of the MNPs the same method was applied as described in the experimental part. Such purified MNP-OCL materials were

![Fig. 2: Representative TEM images of coated nanoparticles taken at different magnifications. The white frames in (a, c, e and g) show the area of zoom which are displayed in (b, d, f and h). The white arrows indicate the thickness of the polymeric coating. (a) MNP-OCL, (b) zoom in MNP-OCL, (c) MNP-OPDL, (d) zoom in MNP-OPDL, (e) MNP-OCL-OPDL, (f) zoom in MNP-OCL-OPDL, (g) MNP-OPDL-OCL and (h) zoom in MNP-OPDL-OCL.](image-url)
analyzed again by TGA. Here the mass loss related to the polymeric part was found to be around 20 wt%, which is somehow in agreement with the theoretical considerations based on the dimension determined in TEM experiments.

The FTIR results indicate successful ROP of OCL or OPDL (Fig. 3) onto single modified MNP-OPDL and MNP-OCL, respectively, as previously reported in references [26] and [24]. A strong signal was observed at 1721 cm⁻¹, which can be attributed to the carbonyl bond (C=O) of OCL and OPDL segments in both MNP-OPDL-OCL and MNP-OCL-OPDL. Another two bands in the range of 1155 and 1293 cm⁻¹ can be assigned to the C–O and C–C stretching in the amorphous and crystalline phases of OCL and OPDL in coatings of MNPs [41].

The degrafted oligomeric polyesters were explored by GPC and ¹H-NMR. The determined $M_n$ of the detached oligomeric coatings from GPC measurements are listed in Table 1. The detached polymeric coatings of MNP-OCL-OPDL exhibited a $M_n$ of 7400 g·mol⁻¹, which is almost three-fold of the starting single coated MNP-OPDL (2500 g·mol⁻¹), and the polydispersity (PDI) was found to decrease from 3.1 to 1.7. Similarly, an increase in $M_n$ from 1700 to 5300 g·mol⁻¹ was observed for MNP-OPDL-OCL after coating with OPDL, while the PDI decreased only slightly from 2.3 to 2.1. The increase in $M_n$ confirms a successful synthesis of OCL-OPDL and OPDL-OCL layers on MNP surfaces.

Table 1: Thermal properties and degree of crystallinity of functionalized MNPs, determined or calculated from DSC data and number average molecular weight ($\tilde{M}_n$) and polydispersity of detached oligomeric coating from MNPs, measured using GPC or ¹H-NMR, as well as crystal length of MNPs, determined by WAXS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_m,_{OCL}$</th>
<th>$T_m,_{OPDL}$</th>
<th>$\Delta H_m,_{OCL}$</th>
<th>$\Delta H_m,_{OPDL}$</th>
<th>$X_{c,_{OCL}}$</th>
<th>$X_{c,_{OPDL}}$</th>
<th>$\tilde{M}_n$</th>
<th>PDI</th>
<th>$M_n$</th>
<th>$l_{c,110}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MNP-OCL</td>
<td>52 ± 1</td>
<td>–</td>
<td>72</td>
<td>–</td>
<td>53</td>
<td>–</td>
<td>1300</td>
<td>2.3</td>
<td>4000</td>
<td>23.5</td>
</tr>
<tr>
<td>MNP-OPDL</td>
<td>–</td>
<td>89 ± 1</td>
<td>–</td>
<td>34</td>
<td>–</td>
<td>27</td>
<td>2500</td>
<td>3.1</td>
<td>2000</td>
<td>20.9</td>
</tr>
<tr>
<td>MNP-OCL-OPDL</td>
<td>50 ± 1</td>
<td>83 ± 1</td>
<td>55</td>
<td>15</td>
<td>41</td>
<td>12</td>
<td>7400</td>
<td>1.7</td>
<td>3900 (2900)</td>
<td>17.2</td>
</tr>
<tr>
<td>MNP-OPDL-OCL</td>
<td>49 ± 1</td>
<td>85 ± 1</td>
<td>66</td>
<td>1</td>
<td>49</td>
<td>1</td>
<td>5300</td>
<td>2.1</td>
<td>4900 (3700)</td>
<td>19.1</td>
</tr>
</tbody>
</table>

* $T_m$ and $\Delta H_m$ from the 2nd heating run of DSC analysis.
* $X_c$ calculated from DSC data by eq. (5).
* $\tilde{M}_n$ obtained from GPC.
* $\tilde{M}_n$ obtained from ¹H-NMR (partial $\tilde{M}_n$ of OCL in brackets).
* $l_{c,110}$ was calculated from WAXS by eq. (4).
In Scheme 2 the chemical structure of the degrafted oligomers is displayed, indicating chemically different hydrogen atoms related to characteristic \( ^1H \)-NMR signals. The black solid line in Fig. 4 shows the obtained \( ^1H \)-NMR spectra with the characteristic peaks for OCL at 4.01 (t, CH\( _2 \)O), 2.25 (t, CH\( _2 \)CO), 1.60 (t, CH\( _2 \)a), 1.34 (t, CH\( _2 \)b), 4.25 (m, CH\( _2 \)O) and 2.61 (m, CH\( _2 \)COOH), while the characteristic peaks for OPDL at 3.98 (t, CH\( _2 \)O), 2.21 (t, CH\( _2 \)CO), 1.54 (t, CH\( _2 \)b), 1.18 (t, CH\( _2 \)c), 4.24 (m, CH\( _2 \)O) and 2.72 (m, CH\( _2 \)COOH) are represented by the gray solid line, which are in good agreement with earlier reported values for PCL and PPDL [42–44]. Detached diblockcopolymers (OCL-OPDL and OPDL-OCL) show, as expected, mixed signals of both oligomers in the spectra (black dashed line and gray dotted line). By comparing the ratio between the integral of peak \( g \) (I\( g \)) and the integral of peak \( c \) (I\( c \)) and peak \( f \) (I\( f \)), respectively, the number of repeating units (\( n \)) can be calculated as shown in eqs. (1) and (2). Number average molecular weights (\( M_n \)) were calculated according to eq. (3), in which the molecular weight for \( \varepsilon \)-caprolacton (CL) is \( M_{CL} = 114 \text{ g·mol}^{-1} \), while \( M_{PDL} = 240 \text{ g·mol}^{-1} \) for \( \omega \)-pentadecalactone (PDL). Table 1 summarizes the results for the calculation of \( M_n \) from \( ^1H \)-NMR spectra. \( M_n \) of 4000 g·mol\(^{-1}\) for OCL and 2000 g·mol\(^{-1}\) for OPDL were obtained from eq. (1) to (2). Based on eq. (3) the overall molecular weight of OCL-OPDL was calculated to 3900 g·mol\(^{-1}\) (\( M_{n,OCL} = 2900 \text{ g·mol}^{-1} \) for

**Scheme 2:** Structure of degrafted oligomers indicating designation of hydrogen for \( ^1H \)-NMR analysis, (a) OCL, (b) OCL-OPDL, (c) OPDL and (d) OPDL-OCL.

**Fig. 4:** \( ^1H \)-NMR spectra of degrafted oligomers OCL (solid black line), OCL-OPDL (dashed black line), OPDL (solid gray line) and OPDL-OCL (gray dashed line).
OCL layer and \( M_{n,\text{OPDL}} = 1000 \text{ g·mol}^{-1} \) for OPDL layer) and for OPDL-OCL the calculated \( M_n \) was 4900 g·mol\(^{-1} \) (\( M_{n,\text{OPDL}} = 1200 \text{ g·mol}^{-1} \) and \( M_{n,\text{OCL}} = 3700 \text{ g·mol}^{-1} \)). Sn(Oct)\(_2\) is generally known as coordination-insertion catalyst [45]. Transesterification reactions, which would adulterate the intended bi-layered structure, are therefore unlikely. However, to examine this, additional \(^{13}\text{C}-\text{NMR}\) spectra were recorded to investigate the sequence structure of the proposed diblock copolymers. In order to do this, the signals at \( \sim 64\text{ ppm} \) of carbon atoms as assigned with “a” or “A” in Scheme 2 were considered to determine the diad abundance of the oligomers as described in [46]. Doing so, it was found that the according diad PDL-CL for the junction site of OPDL-OCL occurs to an extend as expected from the number of repeating units calculated from \(^1\text{H}-\text{NMR}\) spectra, whereas the signals of the reverse diads is negligible (data not shown). However, considerable transesterification was found for OCL-OPDL. This might be caused by the very long reaction time for the ROP of PDL as graft from the existing MNP-OCL.

The crystal structures of uncoated and oligomer functionalized MNPs were investigated by WAXS and the resulting scattering curves are displayed in Fig. 5. For pure MNPs, the position and relative intensities of all peaks (data not shown here) matched well with the reported characteristic diffraction peaks (220), (311), (400), (422), and (511) of the inverse cubic spinel structure of crystalline magnetite [9, 24]. In addition to the magnetite peaks, the single and double-layer coated MNPs displayed a main diffraction peak around \( 2\theta = 21.5^\circ \), which can be attributed to the (110) planes of the orthorhombic crystal structure of OCL [26] as well as OPDL [24]. This diffraction peak was utilized for the determination of the lateral crystal size \( l_c \) of the oligomeric coatings. In comparison with single-layer coated MNP-OCL and MNP-OPDL, the incorporation of the second layer (OPDL or OCL) decreased the overall lateral crystal size from 23.5 nm to 17.2 nm, as shown in Table 1. This demonstrates, similarly to the DSC results, that the crystallization ability of OCL and OPDL segments in bi-layered MNPs was weaker than those in single-layer MNPs. The reason could be that the ROP reaction of the second layer, initiated from the end groups of the OCL or OPDL segments in the first layer, destroyed their previously formed crystals in the first layer or a change in the composition of the first coating by spontaneous transesterification reactions which are known to be supported by high temperatures. In addition, in both inner and outer layers in bi-layered MNPs, the crystallization abilities of OCL and OPDL segments were restricted by the covalent connection between each other.

Figure 6 shows the DSC heating curves of MNP-OCL, MNP-OPDL-OCL, MNP-OPDL, and MNP-OCL-OPDL obtained in the 2nd heating run. For both single-layered MNPs only a single melting transition (\( T_m \)) is observed either at 52 °C, attributed to melting of OCL crystallites (\( T_m,\text{OCL} \)) in MNP-OCL or at \( T_m,\text{OPDL} = 89^\circ \text{C} \) related to melting of OPDL crystallites in MNP-OPDL. The MNPs comprising the two-layered shell show two well separated \( T_m \)s with characteristic melting peaks of OCL and OPDL segments in the DSC curves. For MNP-OPDL-OCL two distinct peaks were found whereby the peak maximum of the melting transition was shifted to
slightly lower temperatures of $T_{m,OCL} = 49 ^{\circ}C$ and $T_{m,OPDL} = 85 ^{\circ}C$. In contrast, MNP-OPDL-OCL exhibited only a pronounced melting peak related to the OCL crystalline phase at 50 °C (see Fig. 6a), while the small melting peak attributed to the OPDL crystalline domains at 83 °C becomes only obvious in the enlarged Fig. 6b. In all obtained DSC curves no pronounced glass transition temperature, related to the change of the amorphous domains from the glassy to the rubbery state, could be observed for OCL or OPDL.

More importantly, as summarized in Table 1, the crystallinity of the OCL domains $X_{c,OCL}$ in MNP-OCL-OPDL (41 %) is lower than $X_{c,OCL}$ of MNP-OCL (53 %), indicating that the addition of the second OPDL layer reduced the degree of crystallinity of OCL as the inner layer. In contrast a tremendous reduction in $X_{c,OPDL}$ from 27 % (MNP-OPDL) to 1 % for the bi-layered MNP-OPDL-OCL was observed, which is in agreement with the low amount of PDL found for detached bi-layers via NMR. A suitable explanation for this change in $X_{c,OPDL}$ might be a removal of a substantial amount of free OPDL oligomers, from the mixture of oligomers and monolayer functionalized MNPs obtained after the first ROP when conducting the second ROP. Furthermore, the Sn(Oct)$_2$ catalyst may cause a potential depolymerization of the established OPDL or transesterification reactions during ROP of the second OCL layer.

**Summary and conclusions**

In this paper, we explored whether hybrid precursors comprising an inorganic magnetic core surrounded by two different subsequent polymeric layers can be prepared by a two-step surface initiated ROP of MNPs using Sn(Oct)$_2$ as coordination-insertion catalyst. FTIR, DSC, TGA and WAXS results indicated that a second OPDL or OCL layer could be grafted from the previously generated OCL or OPDL functionalized MNPs. While TGA results indicated an almost identical two-step degradation behavior of both bi-layered systems, DSC experiments revealed a tremendously lower crystallinity of the OPDL segments in MNP-OPDL-OCL. GPC measurements and $^1$H-NMR results revealed an increase in the number average molecular weight of the detached oligomers after conducting the second ROP. Further NMR analysis of the degrafted bi-layered oligomers confirmed the presence of both OCL and OPDL moieties, while only a few $\omega$-pentadecalactone repeating units are present and transesterification was caused by the 2$\text{nd}$ ROP. This observation is supported by a low degree of crystallinity for OPDL in the degrafted oligomeric bi-layers as found in WAXS and DSC experiments. TEM images confirmed a successful covalent attachment of oligomeric shells to the iron oxide core, whereby an unexpected reduction of the shell thickness by adding the second oligomeric layer was found. In summary these results suggest that Sn(Oct)$_2$ was not a good choice as catalyst for the preparation of bi-layered coated MNPs. Additionally, the large discrepancy of the theoretical thicknesses of the grafted oligomeric shell, calculated from the mass composition obtained by TGA, to results achieved from TEM analysis, led to the
conclusion that besides the grafted nanoparticles also non-grafted single OCL or OPDL oligomers or cooligomers are formed, which could not be completely removed by the selected MNP purification procedure.

Based on the findings achieved with complementary analytical methods, we were able to identify the major challenges in the two-step ROP based synthesis of hybrid MNP precursors with two different polymeric layers, which are the selection of a suitable catalyst as well as the great importance of the applied purification procedure for removal of free oligomers.

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