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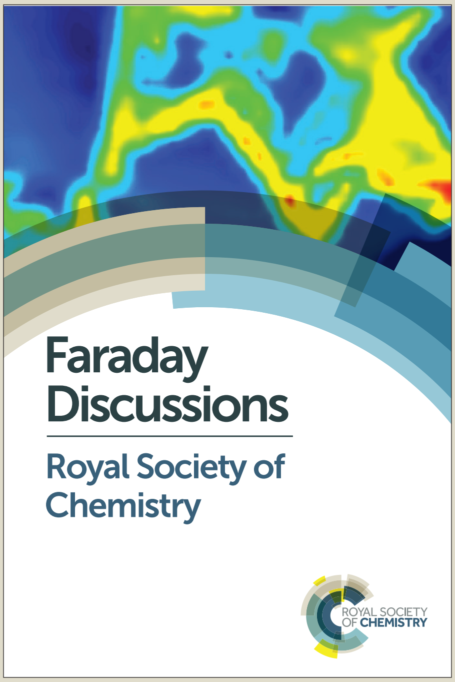

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From near hard spheres to colloidal surfboards

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This work revisits the synthesis of the colloidal particles most commonly used for making model near hard suspensions or as building blocks of model colloidal gels, i.e. sterically stabilised poly(methyl methacrylate) (PMMA) particles. The synthesis of these particles is notoriously hard to control and generally the problems are ascribed to the difficulty to synthesise the graft stabiliser (PMMA-*g*-PHSA). In the present work, it is shown that for improving the reliability of the synthesis as a whole, control over the polycondensation of the 12-polyhydroxystearic acid is the key. Changing the catalyst and performing the polycondensation in the melt, the chain length of the 12-polyhydroxystearic acid is controlled better, as confirmed by ^{1}H-NMR spectroscopy. Control over the graft copolymer now enables us to make small variations of near hard sphere colloids, for example spherical PMMA particles with essentially the same core size and different thickness of the stabilising layer can now be readily produced, imparting controlled particle softness. The PMMA spheres can be further employed to create, on gram scale quantities, colloidal building blocks having geometrical and/or chemical anisotropy by using a range of mechanical deformation methods. The versatility of the latter methods is demonstrated for polystyrene latex particles as well.

1 Introduction

Over the past few decades, the study of model colloidal dispersions has shown to be essential in furthering our understanding of a wide range of physical phenomena and engineering problems. Pusey and van Megen, as early as 1986, demonstrated that suspensions of sterically stabilised poly(methyl methacrylate) (PMMA) colloids exhibited nearly perfect hard sphere equilibrium phase behaviour, with the volume fraction being the single control parameter.[1,2] A key feature for having near hard sphere behaviour was the presence of a short, dense brush of polyhydroxystearic acid on the particles of sufficient large diameter (in the micrometer range). Further studies showed how modulating this near hard sphere behaviour leads to changes in properties, for example various aspects of the rheology can be tailored introducing softness or weak attractions.[3] These observations increased the efforts to produce colloids with varying softness, of different shapes and directional interactions or a combination of those,[4–11] to further the array of colloidal building blocks employed to engineer colloid based soft matter.

Poly(methyl methacrylate) (PMMA) particles sterically stabilised with poly(methyl methacrylate)-*graft*-polyhydroxystearic acid (PMMA-*g*-PHSA) have been used as models to mimic atomic systems.[12] The phase transitions, the equation of state and the divergence of viscosity with increasing volume fraction can be captured by hard sphere behaviour.[13] The colloidal scale enables studies of an array of fundamental phenomena, such as nucleation and crystalization[14–16], disclocation dynamics[17] glass transitions,[15,16] flow in glasses[18], and gelation[19,20] by relatively simple techniques such as light microscopy and scattering.

These particles are produced by a notoriously difficult to reproduce and control dispersion polymerisation. The synthesis was introduced during the 1970's,[4,21,22] but the one step procedure described by Antl *et al.*[23] is the most commonly used.[24–29] Recently, Elsesser and Hollingsworth reviewed the synthesis of the graft polymer stabiliser, PMMA-*g*-PHSA, pointing out the difficulties in its preparation and the importance of its properties in the dispersion polymerisation.[25] They showed that the graft copolymers manufactured in different labs, according to similar or even identical procedures, are not equally efficient in the production of the particles. One is thus left with an uneasy feeling that the most popular model system in colloid science is rather difficult to obtain with sufficient control.

The stabiliser is generally produced in three steps:[25]

I polycondensation of 12-hydroxystearic acid (HSA) to produce the "teeth" of the comb-like graft polymer;
II conversion of the 12-polyhydroxystearic acid (PHSA) with

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glycidyl methacrylate (GM) to yield a PHSA-GM and
III synthesis of the PMMA backbone and simultaneous incorporation of the PHSA-GM polymer.

The first step, which is the most crucial step of the synthesis of the graft polymer, is done in solution and the water formed during polycondensation is removed as an azeotrope, typically using a Dean-Stark apparatus. Both, catalysed reactions, using methanesulfonic acid or tin(II)chloride, and noncatalysed reactions at higher temperature have been employed, none giving satisfactory control. Most surprisingly it is typically recommended to carry out the polycondensation with technical grade 12-hydroxystearic acid, as higher purity leads to poorer control of the PHSA.[25]

The second aspect that makes the poly(methyl methacrylate) (PMMA) particles stabilised with PMMA-g-PHSA interesting is the possibility to deform them into anisometrically shaped colloids. The method to produce ellipsoids out of spherical PMMA particles was first introduced by Keville *et al.*[30] They embedded the colloids in a cross-linked polydimethylsiloxane (PDMS) film that was then uniaxially stretched at temperature above the glass transition temperature (T_g) of poly(methyl methacrylate). After the cooling and subsequent degradation of the matrix they recovered highly monodisperse prolate ellipsoidal particles. This procedure is robust and ensures relatively high yield. Moreover, it helped create another type of colloids which can be considered a model system for the investigations of the particles shape effects.[31,32] Various methods for producing anisotropic particles have been proposed since then, which include making oblate particles[10,33,34] or even chemically patterned anisotropic particles.[32] PDMS cannot be used for hydrophilic particles, as they cannot be dispersed in it. This issue was resolved by Ho *et al.*[35] who produced ellipsoidal particles by uniaxial stretching of poly(vinyl alcohol) (PVA) films loaded with sulfonated polystyrene (PS) particles. The range of particles shapes obtainable was expanded by employing biaxial stretching[10,33] and adding chemical liquefaction of the PS particles to the the stretching procedure.[36]

The aim of the present work is to first and foremost optimise the synthesis of the graft stabiliser PMMA-*g*-PHSA in order to facilitate reproducible and controlled production of spherical PMMA particles, beyond hard spheres. Second we will describe methods for making large quantities of a variety of model anisotropic particles, beyond ellipsoids. The paper is divided into four sections. The first part focuses on the production and characterisation of the comb-like polymer (PMMA-*g*-PHSA) which is being used as the stabiliser of the particles. ^{1}H-NMR spectroscopy is used to monitor the polycondensation of the 12-hydroxystearic acid in detail, the methods to suppress the side reactions during the polycondensation with the goal of being able to vary the chain length of the PHSA chains on the graft copolymer. Next, the different comb polymers are used to make particles with different stabiliser layer thicknesses. The third section is devoted to the characterisations of the colloidal particles and briefly compares the effect of the length of the PHSA chains. The final part of the paper presents methods for producing gram scale quantities of disk-like (oblate ellipsoids) and surfboard-like (triaxial) particles.

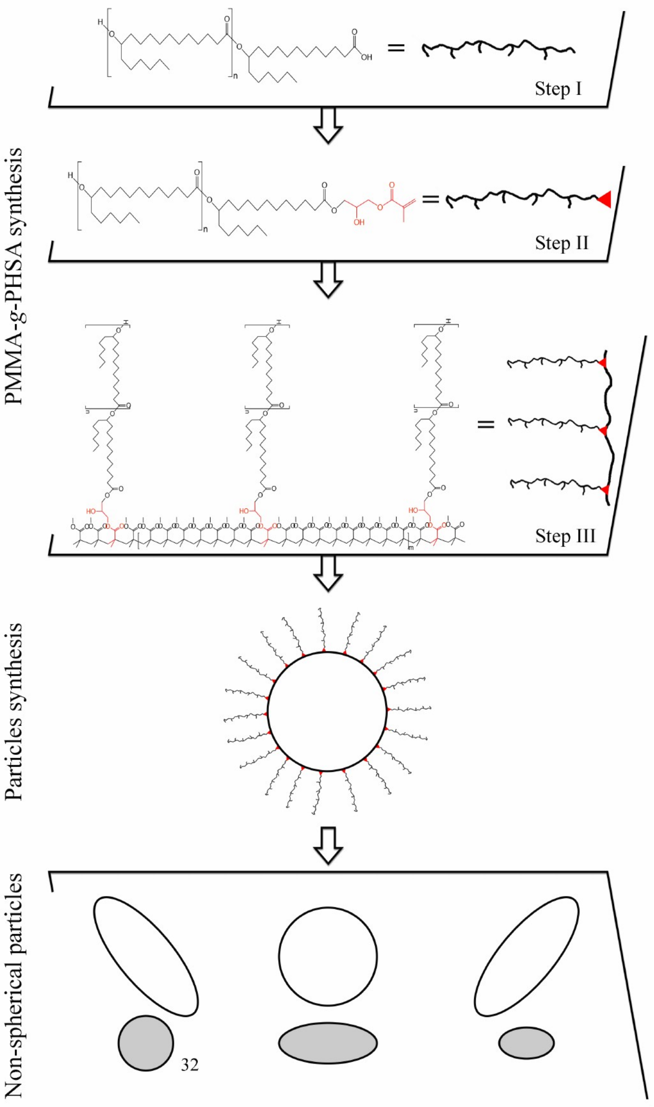

Fig. 1 Schematic depicting the structure of this synthesis and particle production. The first part deals with the synthesis of the graft polymer that is used for PMMA particles production. The spherical particles are further deformed into ellipsoids (see ref.32), disk-like and surfboard-like particles (top view and cross sections in grey).

2 Materials and methods

2.1 Stabiliser and particles synthesis

For the synthesis of the 12-polyhydroxystearic acid (PHSA), two grades of 12-hydroxystearic acid (HSA) were employed: 95% purity (Alfa Aesar, Karlsruhe, Germany) and >75% purity (TCI Deutschland GmbH, Eschborn, Germany). The reaction was catalysed with *p*-toluenesulfonic acid (TSA) or methanesulfonic acid (MSA) from Sigma-Aldrich. Glycidyl methacrylate (97%) (GM) was purchased from Acros Organics and used as received. Since the stability of the epoxy ring is crucial in the synthesis of the PMMA-g-PHSA, the glycidyl methacrylate was examined by

^{1}H-NMR spectroscopy prior to use. Monomers methyl methacrylate (MM) and methacrylic acid (MA) were also products of Acros Organics. Methyl methacrylate was distilled before it was used, but methacrylic acid was not further purified. The solvents *n*-dodecane, *n*-hexane and *n*-butyl acetate were purchased from Sigma-Aldrich, while toluene came from Acros Organics and ethyl acetate from Fischer Scientific UK. All the solvents had highest available purity. A radical scavenger *t*-butyl catechol (*t*BC) and a chain transfer agent 1-octanethiol were also received from Sigma-Aldrich. The reaction between PHSA and glycidyl methacrylate was catalysed by 1-(dimethylamino)dodecane (DDA) purchased from Fluka. The initiator in the polymerisation of methyl methacrylate, azobisisobutyronitrile (AIBN) (Fluka), was recrystallised from acetone before usage.

The first step of the stabiliser synthesis, i.e. polycondensation of 12-hydroxystearic acid, is the most critical. An essential aspect for controlling the polycondensation is efficient water removal from the reaction mixture. When the reaction was performed in solution with toluene as a solvent, as in the reference method described in literature,[25] water was removed using a Dean-Stark apparatus. For comparison the reactions were also carried out in the melt state. Additionally different catalysts were used, and we compared the efficiency of methanesulfonic and toluenesulfonic acid. In these cases vacuum (10^{-3} mbar) or strong nitrogen flow (1.35 l/h) were used for removing the water formed during polycondensation. In all three protocols, the reaction temperature and the monomer/catalyst ratios were varied in the range 100-150°C and 68-811 (wt/wt), respectively, in order to find reliable conditions which favour the main polycondensation reaction. The average number molecular weight of the molecules was based on the analysis of ^{1}H-NMR spectra.

For the second step, i.e. reacting glycidyl methacrylate with the different PHSAs to prepare for attachment to the back-bone of the comb, we modified the reference procedure given in Hollingsworth and Elsesser[25], by using a better method for water removal and by using the ^{1}H-NMR results to calculate, for each chain length, the required quantities of PHSA/GM. Briefly, 3 g of PHSA with 5.1 monomer units was weighed into a reaction flask and placed in an oil bath heated to 140 °C. Once the PHSA has melted, a mixture of toluene (1.1012 g), glycidyl methacrylate (0.3324 g), 1-dimethylaminododecane (16μl) and t-butyl catechol (0.0052 g) was added to the PHSA. The flask was connected to a reflux condenser and a nitrogen line which facilitated water removal with nitrogen flow of 0.084 Nl/min. The refluxing took 7 hours and the reaction progress was followed by analysing the ^{1}H-NMR spectra of the samples taken every hour. During the cooling process 2.2 g of toluene were added to compensate for the solvent that was lost during the reaction and to dilute the product to $\sim$50 wt%. The exact concentration of the solution was determined by drying and weighing a small aliquot and the product was stored in a refrigerator.

In the third step, the stabiliser is connected to a PMMA backbone and a comb-copolymer was made using the standard procedure[25] and taking into account the variation in the molecular weight of the PHSA. Methyl methacrylate was first mixed with the initiator (AIBN) and then the product of the second step (toluene solution of PHSA-GM) was introduced. The mixture was put in a glass syringe and within 2-3 h added to the reaction flask containing a mixture of ethyl acetate and butyl acetate in ratio 2:1 (wt/wt) and heated to 108 °C. The molar ratio between methyl methacrylate and PHSA-GM was kept between 13 and 15.5. The amount of AIBN was calculated based on the amount of methyl methacrylate; for every gram of methyl methacrylate, 0.017 g of initiator was used. Furthermore, the mass of the acetate mixture was 1.14 times higher than the mass of methyl methacrylate. Once the content of the syringe was completely transferred to the reaction flask, the refluxing continued for 6 additional hours. Within that time the initiator was added two times at intervals of 2 h. The respective aliquots were 2.2 times smaller than the amount added in the initial mixture. When the reaction was finished and the temperature lowered to about 80 °C, the product was diluted with ethyl acetate/butyl acetate mixture in order to avoid micelle formation which can occur when the concentration of the graft polymer exceeds 40 wt%.[37] The mass of the added ethyl acetate was equal to the mass of MM and the amount of butyl acetate was half the mass of methyl methacrylate. The exact concentration of the stabilisers was determined by drying and weighing small aliquots of the solutions.

The PMMA particles were then produced following the procedure of Klein *et al.*.[38] Hexane and dodecane were weighed into a 3-neck reaction flask in a ratio 2:1 (wt/wt) and then the stabiliser solution was added to the mixture. The monomers methyl methacrylate and methacrylic acid were weighed in a beaker in a weight ratio 98:2. The initiator and chain transfer agent were mixed with the monomers and added to the reaction flask placed above an oil bath heated to 95 °C. Once the AIBN was completely dissolved, the 3-neck flask was lowered into the oil bath and the reaction was allowed to proceed for 2 hours. When the mixture was cooled down to room temperature, the particles were filtered and washed extensively with heptane and dodecane. After five washings, the solvent was replaced with decalin.

2.2 Producing oblate ellipsoids and surfboard-like particles

Poly(methyl methacrylate) (PMMA) particles. To produce the films the particles were embedded into polydimethylsiloxane (PDMS) films by adjusting the procedure introduced by Keville *et al.*[5] and later improved by Mohraz *et al.*[31] and Zhang and the collaborators.[32] In our specific case, polydimethylsiloxane ($M_n \sim$100000, viscosity $\sim$50000 cSt, Sigma-Aldrich) was first mixed with *n*-heptane (Acros Organics) in 1:2 (wt/wt) ratio. The particles were added to the PDMS/*n*-heptane mixture as a 6 wt% suspension in *n*-heptane. Poly(dimethylsiloxane-*co*-methylhydrosiloxane) (trimethylsilyl terminated, $M_n \sim$950, Aldrich-Fine Chemicals), and the catalyst, tin(II) 2-ethylhexanoate (Aldrich-Fine Chemicals) were introduced. Both chemicals were first dissolved in few ml of *n*-heptane. The amount of cross-linker and catalyst was based on the mass of PDMS and it was 0.3 and 0.36 wt%, respectively.[32] After adding all the components, the mixture was vigorously shaken and poured into circular Teflon mold(s) each with diameter of 12 cm and left at room temperature for about 20 hours. During this time the solvent evaporated completely and precured films were formed. The films were then cured in a vacuum oven at 120 °C and 4 mbar for 6 hours. This resulted in ~800 μm thick rubbery PDMS film(s). In order to produce 6 of these sheets, 65.5 g of PDMS was needed. To test the production of the particles, two batches with different stabilisers, but with approximately same size ~2 μm, were compared.

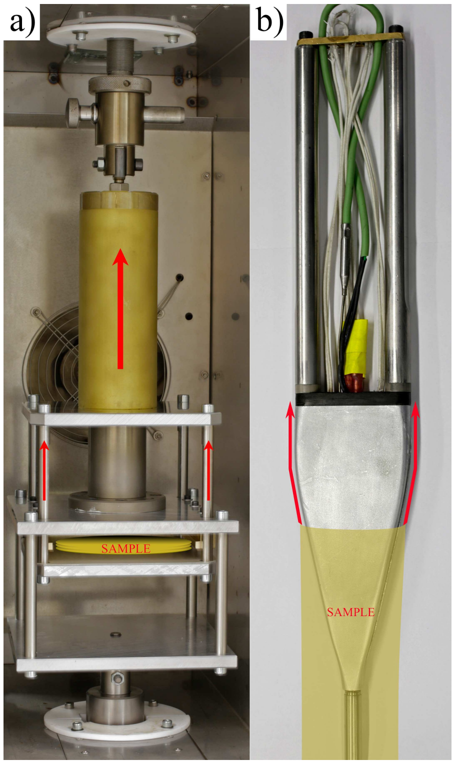

Fig. 2 Geometries for thermo-mechanical deformation of the latex particles a) lubricated compression b) plastic drawing of a particle-filled polymer tube over a heated fork.

Before deformation, the edges of the films were removed and circular films with a diameter of 10 cm were made. The disk-like particles were obtained by lubricated compression of particle filled PDMS films using a Zwick/Z020 (Zwick Roell Group) as a mechanical platform. For this, a new geometry was designed in-house (Figure 2a)). The top and the bottom surface were lubricated with fluoroether based grease (Krytox, DuPont) to ensure uniform deformation of the films. The compression was carried out at 160°C, well above the glass transition temperature (T_g) of PMMA. The whole procedure consisted of five steps. First, the setup was preheated to 160°C. Once the temperature is reached, the PDMS is placed on the bottom plate of the lubricated geometry (see Figure 2). The sample was conditioned for 15 minutes. The next step was applying predefined force, which was chosen based on the desired final aspect ratio. The films were kept under constant force (<±5%) for 7 h, the magnitude of the force depending on the diameter of the films and the desired aspect ratio. In the first hour the temperature was kept at 160°C and then the sample was slowly cooled down to room temperature. Since the PDMS exhibits rubber-like behaviour, the films had to be kept under stress while cooling to ensure that the particles keep the new shape. After deformation, the sample was placed between absorbing paper sheets to remove some of the lubricating oil residues. Additionally, the films were soaked in perfluoroheptane for 5-10 minutes which sufficed to remove all traces of Krytox oil. In order to avoid the edge effects, 2-3 mm were removed from the edges. Before proceeding to the degradation step, the PDMS sheets were weighed, cut into ~1 cm^2 pieces and swollen in *n*-hexane or *n*-heptane for 24 h.

The procedure to make the surfboards is essentially the same, but the films are now produced in a rectangular through. After removing the edges the films are cut in 2 cm wide strips and they are compressed in lubricated channel dies of the same width.

A degrading reagent for PDMS is sodium methoxide. Similar to the procedure shown by Zhang, *et al.*[32] a 0.22 wt% stock solution of Na-methoxide in isopropanol and methanol was prepared. This was done by dissolving sodium in methanol to obtain 0.5 M solution of Na-methoxide in methanol and by further dilution with isopropanol to the final concentration of 0.22 wt%. A given amount of the stock solution was added to the 4.3 wt% mixture of PDMS films and *n*-hexane or *n*-heptane to obtain final component concentration (wt%) of 3.5% PDMS films, 77.9% *n*-heptane (or *n*-hexane), 17% isopropanol, 2% methanol and 0.04% Na-methoxide. The degradation proceeded for at least 15 h before the recovered particles were washed and re-grafted with a fluorescently labeled (with 7-nitrobenzo-2-oxa-1,3-diazol (NBD)) PMMA-g-PHSA (provided by Dr. Andrew Schofield, University of Edinburgh) following the procedure from the work of Zhang *et al.*.[32] The re-grafted particles were washed extensively with heptane and decalin and stored in decalin.

Polystyrene (PS) particles. Due to the hydrophilic nature of the highly charged sulfate-PS particles, the particles were embedded into a polyvinyl alcohol (PVA) films. In order to obtain an 80 μm thick film of 36x32 cm^2, 12 g of matrix polymer (Mowiol 40-88, M_w=205000 $\mathrm{g\,mol^{-1}}$, Sigma Aldrich) was dissolved in 480 g of MiliQ water for 24 h and then 3.45 g of 8 wt/v particles (0.99 μm) suspension (Life Technologies) was added. The mixture was poured into a Teflon coated mold and left for drying at room temperature.

The films were cut into strips which were glued into tubes of different initial diameter, which were then deformed by plastic drawing using an in-house designed geometry[39] (Figure 2b)). The working temperature was fixed to 140°C, unless otherwise specified. In our experiments, the initial tube length was fixed to 7 cm, while the diameter was varied from 30 to 50 mm. The film thickness was in the range 0.045 to 0.25 mm before stretching. The tubes were drawn at speed of ~ 1 $\mathrm{m\,min^{-1}}$ and cooled down to room temperature in stretched state to prevent relaxation. The final width of the tubes was 7 cm. The films were cut into ~ 1 $\mathrm{cm^2}$ pieces and degraded in a mixture of water and isopropanol (7/3 v/v). After 12 hours of degradation, the particles were washed three times with the same mixture of water and isopropanol and two times with miliQ water.

2.3 Characterisation

Nuclear magnetic resonance (NMR) spectroscopy: ^{1}H- and ^{13}C-NMR spectra were recorded on Bruker AV300 MHz and AV500 MHz spectrometers, using deuterated chloroform and perdeuterated dimethyl sulfoxide (DMSO), respectively, as solvents.

Gel permeation chromatography (GPC): The average number (M_n) and weight (M_w) molecular mass were determined using gel permeation chromatography (GPC) (GPCmax VE2001, Viscotek) equipped with two sets of detectors TDA302 (Viscotek) and UV Detector 2500 (Knauer). The column was calibrated with polystyrene (PS) and chloroform was used as running solvent.

Dynamic light scattering (DLS): The particles size and stability was followed by dynamic light scattering. An ALV/CGS-3 compact goniometer system (ALV, Langen) connected to an ALV-7004 multiple tau digital real time correlator was used to perform these measurements. The size of the particles was determined by obtaining the correlation function at different angles from 30° to 150° with steps of 10°. Suspension stability was determined by following the changes in the correlation function with time. For the latter set of experiments, the angle was not changed (90°) and between each measurement the waiting time was fixed to 30 minutes.

Rheology: A rotational rheometer (MCR502, Paar Physica) was used with a double wall Couette geometry, thermostated using a Peltier system at 25.0 °C.

Scanning electron microscopy (SEM): The instrument used to acquire micrographs of the particles is LEO 1530 Gemini (Zeiss, Oberkoch). The samples were deposited on silicon wafers and coated with gold or platinum. The working voltage was set to 1 kV. The images were used to determine the particles dimensions.

Confocal laser scanning microscopy (CLSM): A multi-beam confocal scanning system VT-Infinity3 (VisiTech international) is used to perform the confocal imaging. The imaging is done using an EM-CCD camera (ImagEM X2 C9100-23B, Hamamatsu) and Nikon Eclipse Ti-E microscope equipped with a 100x oil immersion objective (CFI Plan Apo λ, 1.45 NA, ∞/0.17, 0.14 mm WD, Nikon). The samples were deposited on a glass cover slip and excited at 488 nm with a solid state laser (Laser engine, VisiTech international).

3 Results and discussion

3.1 Synthesis of the poly(methyl methacrylate)-*graft*-polyhydroxystearic acid (PMMA-*g*-PHSA)

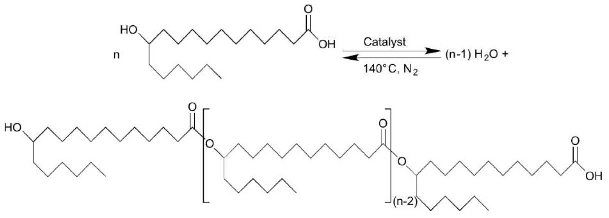

Fig. 3 Polycondensation of 12-hydroxystearic acid.

Step I. In this stage the soluble part of the stabiliser is produced. The esterification reaction between the hydroxy and carboxylic group of the 12-hydroxystearic acid (12-HSA) takes place in the presence of an acid catalyst (Figure 3). The constitutional repeat unit with 12 carbon atoms is linked at the ester bond and has a side chain of 6 carbons atoms. Typically the reaction is carried out in solution either without catalyst, using higher temperature[37,40] or employing methanesulfonic acid (MSA)[23,25,29] or tin(II)chloride[41]. However, the control over this reaction is clearly limited. The most important issues are possible side reactions such as the elimination of water in 12-HSA. In an acid environment, the hydroxyl group on the C_{12}-atom can be removed leaving a double bond between the C_{11}- and C_{12}- or C_{12}- and C_{13}-atom. As the elimination of water is reversible, subsequent addition and elimination of water can lead to a "migration" of the -OH group and of the double bonds, which can change the length of the side chains, and the level of branching. It has been reported that changing the position and/or the length of the branch affects the subsequent particle stability.[42] So it seems that a first key aspect in obtaining a precise control over the stabiliser synthesis, lies in preventing these elimination reactions. Accordingly, emphasis was put on the choice of catalyst.

Esterification reactions are typically catalysed by sulfuric acid, sulfonic acids or Lewis acids. Sulfonic acids are strong organic acids which are readily soluble in organic and inorganic mixtures . For the polycondensation of 12-hydroxystearic acid two acids from the family of sulfonic acids have been mentioned in literature - methanesulfonic acid (MSA)[23,25,29] and toluenesulfonic acid (TSA)[43]. Even though they are very akin, they affect the reaction in different ways. For example, the condensation between lauraldehyde and glycerol was shown to be more efficient when MSA was used as a catalyst instead of TSA under similar reaction conditions.[44] To the best of our knowledge, there is no analogous study for the case of polycondensation of 12-HSA.

Another important aspect in the synthesis of the stabiliser is the removal of the reaction product, water, which is one of the key parameters controlling the chain length. To remove the water, some protocols prescribe carrying out the reaction in solution[23,29], whereas other have performed the reaction in the melt[40,43]. In solution, the water is typically removed by creating an azeotrope from which the water is separated by a Dean-Stark apparatus.[45] When the reaction is performed in the melt, water was removed using vacuum.[43]

Somewhat surprisingly, the majority of the groups, who have synthesised PHSA for the purpose of making near hard sphere particles, seem to agree that technical grade (75-85% pure) 12-hydroxystearic acid leads to better results, when the focus is on making near hard sphere dispersions.[25] The main contaminant in the 12-HSA is stearic acid, but palmitic acid can also be present. These impurities can also participate in the esterification reaction and limit the chain growth (see Elsesser and Hollingsworth[25] for more details), and moreover they affect the branching of the PHSA. Broadening the range of chain lengths that could be produced would facilitate synthesis of PMMA particles of various sizes and different softness levels, but this would be difficult to achieve with the lower grade 12-HSA.

To obtain a deeper insight and better control over the synthesis, we recorded ^{1}H-NMR spectra as a function of reaction time for different reaction protocols. As a reference procedure the most commonly used method of Antl *et al.*,[23] was used. The synthesis is performed using toluene as a solvent with methanesulfonic acid as a catalyst and 12-hydroxystearic acid of 95% purity, of which the ^{1}H-NMR spectra are shown in Figure 4. Samples taken at various reaction times for temperatures ranging from 100°C to 150°C revealed the presence of considerable quantities of olefins, products of the elimination reactions of water, as can be seen in Figure 4b). Varying the temperature at which the catalyst was added also had no significant effect on the suppression of the unwanted side reactions. Following the reports that the reaction in solution is more prone to lactone formation[43] and that production of light coloured (i.e. purer) fatty acid esters of higher alcohols should be done under vacuum to facilitate water removal[46], the polycondensation of 12-HSA was performed in melt under vacuum. However, considerable quantities of elimination products arose also under these conditions (Figure 4c)), and once again varying the temperature and catalyst quantities showed no effect on the final product.

Since further modification of the procedure by employing strong nitrogen flow to remove the water had brought no improvements in the resulting product (Figure 4d)), the focus was turned to the chemical nature of the catalyst.

Toluenesulfonic acid (TSA) has been shown to be an alternate catalyst in the condensation of 12-hydroxystearic acid.[43] **In our experiments, c**atalysis with TSA revealed ^{1}H-NMR spectra of the product with very low quantity of side products, even after 6 hours reaction time at 140°C (Figure 4e)). Note that the only difference in the way the products shown in Figure 4d) and e) were obtained was the catalyst used. Hence, from the NMR data it can be concluded that *p*-toluenesulfonic acid shows higher selectivity in the polycondensation of 12-hydroxystearic acid than methanesulfonic acid. Since the conditions in the polycondensation with *p*-toluenesulfonic acid resulted in a product with very limited amount of olefins, the conditions under which this reaction was carried out were chosen as optimal, i.e. 140°C was set as the reaction temperature and continuous nitrogen flushing as the mean to remove the produced water.

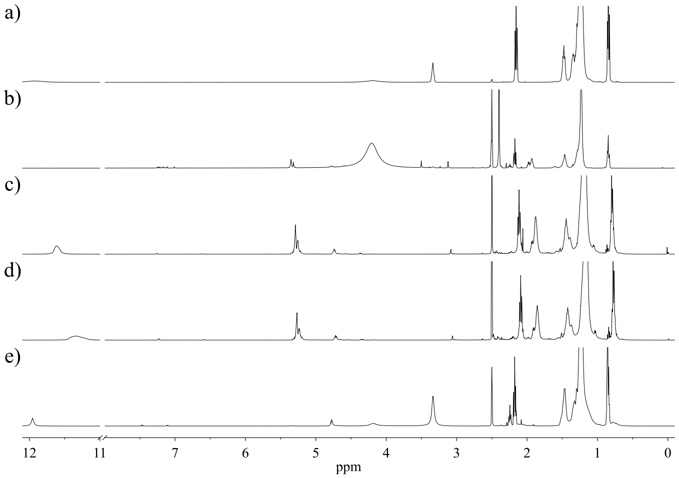

Fig. 4 ^{1}H-NMR spectra of a) the 95% purity 12-hydroxystearic acid and b-e) the products of the different polycondensation protocols. The reaction temperature was 140°C in all cases except in b) where it was 150°C. The products shown in b), c) and d) were obtained after 1 hour using methanesulfonic acid as catalyst. ^{1}H-NMR spectra in e) represent a product of prolonged reaction time (6 h) where the catalyst was toluenesulfonic acid. The amount of catalyst was varied only in b) where it was 1.5 wt% with respect to the monomer, in all other cases it was 0.15 wt%. The water was removed using different methods: b) as an azeotrope with toluene using Dean-Stark apparatus, c) employing vacuum and d) and e) with strong nitrogen flow. The solvent was perdeutareted DMSO.

In literature, the success of the polycondensation reaction was typically determined by titration with alcoholic potassium hydroxide (KOH) solution. However, the precision with which transitions in the titration curves could be detected (either by colour or conductometric), was limited. To investigate the evolution of chain length, as well as the occurrence of side reactions, in more detail we used ^{1}H-NMR spectroscopy. Figure 5 shows the spectra as a function of reaction time from 0 tot 48 hours. The peak at 4.86 ppm in ^{1}H-NMR spectra corresponds to the newly formed ester bond; accordingly this signal is increasing with time. The peak at 3.60 ppm which represents the H-atom at the unreacted C_{12}-atom is decreasing. Another change can be observed in the range of 2.00-2.50 ppm where the signals from the hydrogen atoms at the C_2-atom are positioned. The signal at 2.35 ppm represents a methylene group right next to the carboxyl group in the 12-HSA molecule, while the signal at 2.27 ppm depicts the methylene group next to the ester group. Based on the analysis of ^{1}H-NMR spectra, or more precisely, comparing the integrated intensities of the peaks at 3.60 and 4.85 ppm showed that it took 48 h to obtain PHSA with an average of 5.1 monomer units per chain under the given conditions.

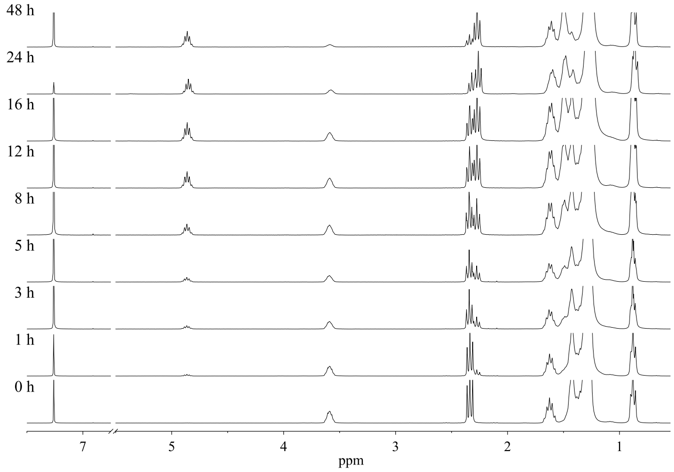

Fig. 5 ^{1}H-NMR spectra of the 95% 12-hydroxystearic acid and the reaction mixtures of different reaction times. The solvent was deuterated chloroform.

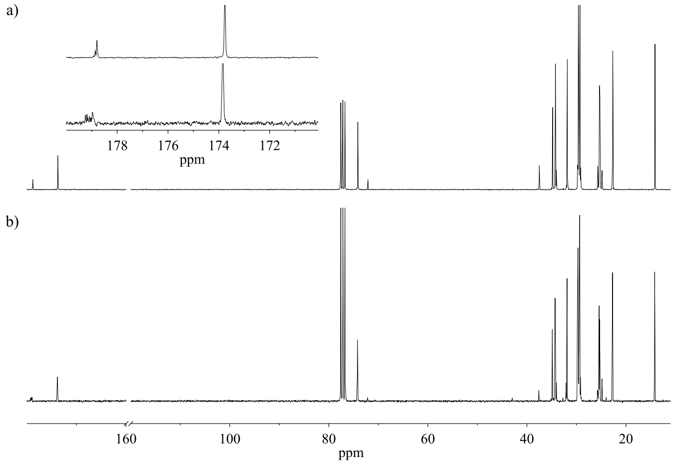

Fig. 6 Comparison of the ^{13}C-NMR spectra of the PHSA produced from the two grades of 12-HSA: a) 95% and b) 75% purity. The inset shows the expansion of the region where the signals of the C-atoms of the carboxyl groups are appearing. The solvent was deuterated chloroform.

The effect of purity was investigated by comparing the results obtained by employing 12-HSA with 75% purity under the same reaction conditions. The ^{1}H-NMR spectra of the two grades of 12-HSA and the products obtained within 48 h showed that the side reactions are suppressed in both cases. The products from both reactions were further compared by performing ^{13}C-NMR spectroscopy shown in Figure 6. In contrast to the literature, where a lower grade 12-HSA is generally considered to yield appreciable results, we found that less pure monomers give ill defined products. Namely, the region between 170 and 180 ppm in the ^{13}C-NMR spectra reveals a range of carboxylic acids present in the sample prepared from the technical grade 12-HSA (inset in Figure 6). As the spectra of the monomers do not show so many peaks in this region, some of the groups were obviously generated during the reaction. This implies that the stabiliser will be composed of a mixture of ester units.

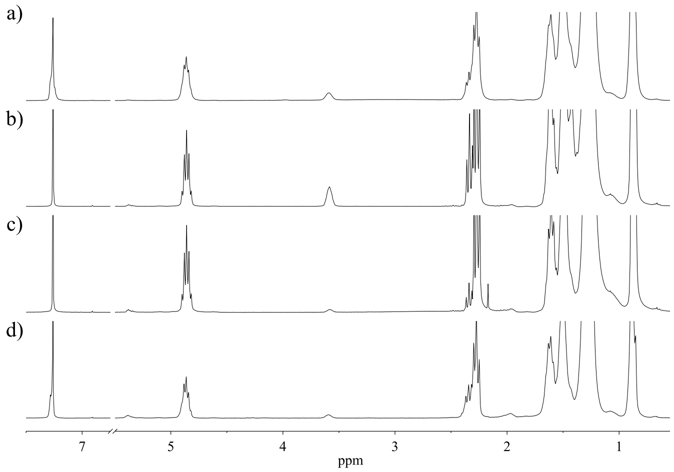

Fig. 7 ^{1}H-NMR spectra of PHSA obtained with different reaction times: a) 48 h reaction time (5.1 monomer units); b) 24 h reaction time (3.6 monomer units); c) 48 h reaction time with addition of catalyst after the first 24 h (15.7 monomer units); d) 48 h reaction time with 12-HSA with 75% purity (11.7 monomer units). The number of monomer units was determined from the ratio of the areas under the peaks indicating the free and -OH groups that entered the ester bond. The solvent was deuterated chloroform.

To verify that the chain length of the PHSA for the pure 12-HSA can be simple controlled by varying the reaction time, additional experiments were carried out. The reaction proceeded for 24 hours under the selected conditions, when half of the reaction mixture was removed from the flask, the amount of TSA was doubled and the reaction was continued for additional 24 hours. Based on the calculations from the recorded ^{1}H-NMR spectra, the product of the first 24 h and the PHSA obtained after additional 24 h with an increased amount of catalyst had 3.6 and 15.7 monomer units, respectively. The ^{1}H-NMR spectra of the two products and the PHSA with 5.1 monomer units as well as the spectra of the product obtained using 75% pure monomer are compared in Figure 7.

Using the ^{1}H-NMR spectra of the samples taken at given time intervals, the conversion rate and reproducibility of the reactions were compared. The diagram in Figure 8 shows how the chain size, as determined from the ratio between the free and reacted hydroxyl groups, changed with time. The repeatability was good. Moreover, the graph depicts that the addition of fresh catalyst has a significant impact on the reaction, in agreement with data from Bawn and Huglin.[43] However, they have observed increase in reaction rate after removing the used and introducing the same amount of fresh catalyst, implying that over time catalyst loses the efficiency.

The ^{1}H-NMR spectra were used to determine the number average molecular weight (M_n) of the different polyhydroxystearic acids. The average number of monomer units per chain of PHSA can be calculated as

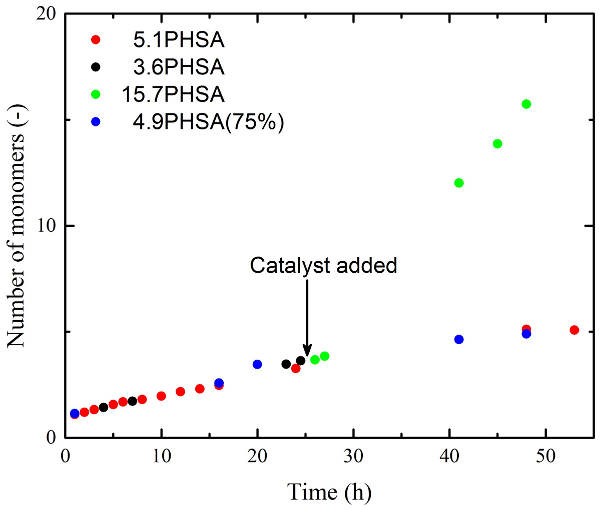

Fig. 8 Progress of the polycondensation reaction of different batches of 12-HSA. Note that the catalyst concentration was doubled after 24 h in the case of 15.7PHSA. 5.1PHSA refers to the sample with a final degree of polymerisation of 5.1, and 3.6PHSA and 15.7PHSA are designated accordingly.

$$\bar{x}_n = \frac{1}{\frac{n_{OH}}{r n_{ester}} + \frac{1}{r} - 1} + 1 \qquad (1)$$

where n_{ester} and n_{OH} represent number of ester and OH-groups, respectively, determined by integration of the corresponding peaks in ^{1}H-NMR spectra. The purity of the monomer is indicated by r which represents the initial ratio of hydroxyl and carboxylic acid groups. The parameter r of the two grades of 12-hydroxystearic acid used in this work was also determined from the ^{1}H-NMR spectra and they were 98% (for the 95% 12-HSA) and 87% (for the >75% 12-HSA). The values of M_n calculated with $r = 1$ and the determined r are included in Table 1.

All the final products of the first step were also analysed by gel permeation chromatography (GPC) to obtain an alternate way to measure the size of the molecules. The number average molecular weights (M_n) determined by this method showed a good agreement with the results acquired by ^{1}H-NMR spectroscopy when the purity of the monomer was taken into account (Table 1). Note that M_n of 15.7PHSA determined by ^{1}H-NMR spectroscopy is subjected to a relatively high uncertainty due to the small interprated intensity of the OH-groups. The polydispersity indices (PDI) obtained by GPC are relatively high which is typical for polycondensation reactions. However, the GPC results should be taken with caution. Namely, the molecular weight curve distribution seems to be composed of several overlapping distributions (Figure 9a)), which makes the determination of M_n less reliable. We performed repeated measurements and checked the effects of small changes in data interpretation on the results obtained from GPC. The collected data showed that the values of peak average molecular weight (M_p) and weight average molecular weight (M_w) were always close to each other and that they were independent of the analysis protocol. However, the number average molecular weight and consequently the PDI varied somewhat depending on the data interpretation.

Another interesting observation is that the sample prepared from the lower grade monomer had no detectable amount of chains with more than 7 monomer units, while the PHSA prepared under the same conditions with purer starting compounds contained significant quantity of longer molecules (Figure 9b)). In addition, as the reaction time was prolonged and the amount of catalyst increased, the fraction of lower molecular weights became insignificant.

Step II. The following reaction in the synthesis of the PMMA-*g*-PHSA is addition of glycidyl methacrylate to the PHSA produced in the first stage. The reaction with the -COOH groups in the polyester takes place in a basic environment, by opening the epoxy ring. For this step, the recipe introduced by Elsesser and Hollingsworth was slightly modified (see "Materials and methods").[25] Due to the previously mentioned difficulties observed with the titration method, here, the number of reacted groups was estimated from ^{1}H-NMR spectra, analogues to the first step. Samples taken at different times were also analysed by NMR spectroscopy to verify that the yield of side products stays within limits of $< 5\%$. Ideally, after the end of the reaction, all the carboxyl groups should disappear and the double bond in the GM should be intact in order to facilitate the following step. In order to verify whether the -COOH groups have reacted, ^{13}C-NMR spectra of the final products were recorded. The PHSAs obtained from the 95% pure 12-HSA with 3.6, 5.1 and 15.7 monomer units were successfully attached to the glycidyl methacrylate permitting the synthesis to proceed to the next step.

Step III. In the final step of the stabiliser synthesis, the PMMA backbone is formed and the PHSA chains are grafted. The backbone can be produced only from methyl methacrylate (MM) or using a mixture of MM and glycidyl methacrylate (GM). The latter is employed when the stabiliser needs to be covalently bonded to the particles surface, which was not a requirement for our study, since the particles during the degradation of the matrix after deformation loose portion of the stabiliser (see "Particles deformation" and Zhang *et al.*[32]). Hence, for simplicity, GM was not included here. Based on the number average molecular weights obtained from the ^{1}H-NMR spectra and the concentrations of the PHSA-GM in the mixture obtained in the Step II, we were able to keep the MM/PHSA-GM molar ratio similar for all three PHSA.

The ^{1}H-NMR spectra confirmed the preservation of the molar ratio of the MM and the PHSA. The molecular weights of the polymers were determined by gel permeation chromatography (Table 2 and Figure 10).The molecular weights of the comb polymer via GPC are only indicative, but it is useful to comapre the values measured with those found in literature; they are in the range M_n=6000-15000 and M_w=20000-35000,[37] with exceptions having a $M_w \sim$60000-75000.[25] Our results agree well with these values, with the exception of the stabiliser that contains the shortest PHSA chains. Considering that the molar

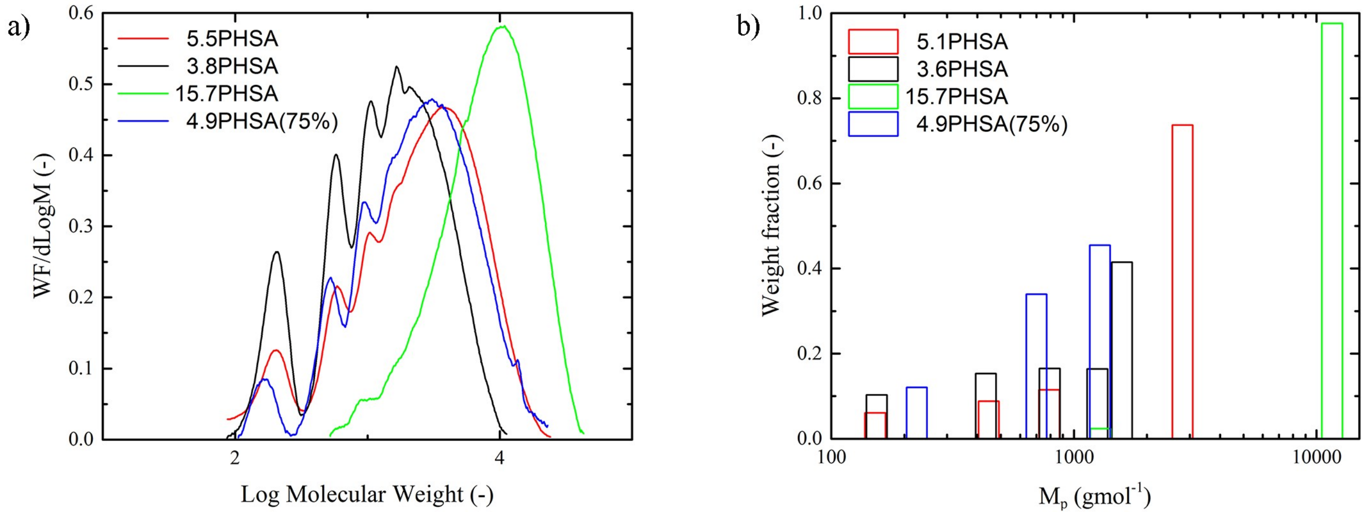

Fig. 9 Gel permeation chromatography results for the PHSA with different chain lengths. a) The molecular weight distribution. b) Weight fractions of certain peak molecular weights in the different samples. Note that some samples show a polymodal molecular weight distribution.

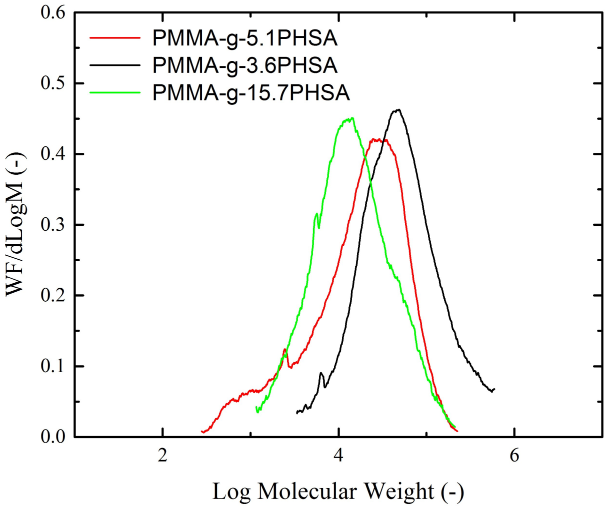

Fig. 10 Molecular weight distribution of the stabilisers containing PHSA with different number of monomer units.

ratio between the methyl methacrylate and PHSA-GM was kept constant, the number of MM molecules in the reaction mixture was the highest in case of the shortest PHSA and vice versa. This can further result in either longer stabiliser molecules or larger number of shorter molecules. The molecular weight distribution curves indicate that the stabiliser chain molecules grow longer with increasing the absolute number of methyl methacrylate units. The efficiency of the produced stabilisers was tested by employing them in particles synthesis.

3.2 Synthesis of spherical particles

The PMMA particles are produced by a dispersion polymerisation.[4] Different groups used various procedures, which mainly differ in the ways the components are added to the reaction mixture.[4,23] Antl *et al.* simplified the synthesis by turning it into a one step procedure, followed by a "locking" step in which the stabilisers was covalently bonded to the particles. Here, the particles were produced by the method of Klein *et al.*,[38] omitting the locking step. Particles were synthesised with the stabilisers containing 3.6, 5.1 and 15.7 monomer units in the PHSA chains. The first batch was produced with PMMA-*g*-PHSA that has the "standard" length - 5.1 monomers. An SEM image of the particles is shown in Figure 11a). Since the results were satisfactory, the amounts of the other stabilisers were calculated in such way that the reaction mixtures contained same number of moles of PMMA backbones with 15.5 monomer units as in the case of the "standard" stabiliser. This should result in same number of PHSA chains per number of MM mols or same grafting density. The micrographs of the particles are presented in Figure 11b and c.

In all three cases stable particles were produced. However, in the case of short PHSA chains, the particles exhibited certain level of roughness. Since the only difference in the three batches is in the length of the soluble moieties, we assumed that the roughness might be caused by a solubility issue. Namely, the PHSA chains are the components that keep the stabiliser dispersed in the hexane/dodecane mixture at the begin ning of the dispersion polymerisation because the PMMA backbone is not soluble in these solvents. Since temperature is one of the parameters affecting the solubility of polymers, the particles synthesis in the presence of PMMA-*g*-PHSA was carried out at different temperatures. This indeed confirmed that the roughness on the particles can be reduced as shown Figure 12. Moreover, these results indicate that it is possible to produce PMMA particles of same size, with controlled level of surface roughnesss, just by varying the reaction temperature. We conducted further tests in order to test the hypothesis that the roughness comes from the stabiliser. The PHSA containing various number of monomer units were dissolved in five solvents with different polarity: hexane ($\varepsilon_r = 1.88$), dodecane ($\varepsilon_r = 2.0$), toluene ($\varepsilon_r = 2.38$), decanol ($\varepsilon_r = 8.1$) and isopropanol ($\varepsilon_r = 18$). As expected,

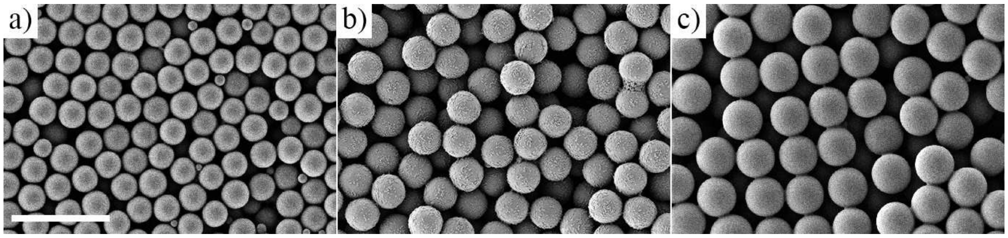

Fig. 11 Particles produced with different stabilisers: a) PMMA-*g*-5.1PHSA, b) PMMA-*g*-3.6PHSA and PMMA-*g*-15.7PHSA. Scale bar is 5 μm.

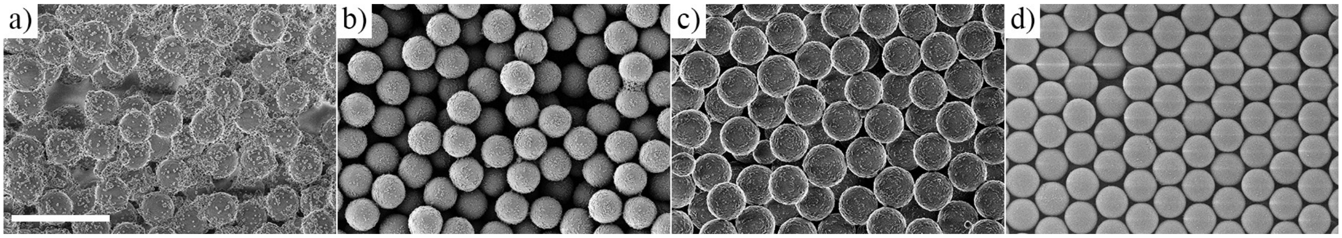

Fig. 12 Effect of reaction temperature on the particles roughness: a) 70°C, b) 95°C and 105°C. All the particles are produced with the stabiliser containing PHSA consisting of 3.6 monomer units. d) The particles synthesised at 95°C after 10 minutes of sonication. Scale bar is 5 μm.

with increasing polarity of the solvent, the solubility of the PHSA with 3.6 monomer units on average was improved. One batch of particles was produced replacing half of the hexane amount with *tert*-butylmethyl ether ($\varepsilon_r = 4.5$). This lead to formation of smooth particles, but significant polydispersity because the specific solvent mixture was partially dissolving PMMA. Interestingly, when the rough particles were subjected to sonication for >10 minutes, great deal of the roughness was removed, but the particles remained stable in suspension (Figure 12d)).

The size of the PMMA particles prepared with different stabilisers was determined from SEM micrographs and by DLS measurements. Since the former gives an estimate of the core diameter and the latter gives the hydrodynamic dimensions, comparing the diameters determined by the two methods allows estimation of the stabilising layer thickness. The results presented in Table 3 show that the calculated hydrodynamic layer thicknesses agree better with the chain length computed based on the number of monomer units in the soluble moieties than with the estimated radii of gyration, indicating that the grafting density is high. Based on a simple mass balance, the grafting densities are estimated to be on the order of 75 $\mathring{A}^2$on average, which agrees rather well with literature values.[47]

Particles stability was tested by DLS and rheology measurements. DLS measurements as a function of extended periods (of days) showed no tendency to aggregated. This suggests that a chain length of 3.6 suffices to produce hard sphere behaviour, meaning that near hard sphere behaviour can be retained to smaller particle diameters as compared to the PMMA-*g*-5.1PHSA. For the rheology measurements, three different volume fractions ($\Phi = 0.04, 0.09$ and 0.16.) were prepared for every particle type. Samples were subjected to an increasing shear rate ($\dot{\gamma}$) until 1000 s^{-1}, when the $\dot{\gamma}$ was decreased until reaching the initial value. All the samples exhibited fully Newtonian behaviour under the chosen shearing conditions, as expected for this range of volume fractions. Moreover, calculated effective volume fractions (from the relative viscosity, using Krieger Dougherty[3]) agreed well with the experimental values for volume fractions, confirming that the particles are exhibiting near hard sphere behaviour.

3.3 Large scale production of non-spherical particles

The production of prolate ellipsoidal particles has been discussed extensively in previous work.[30,32] In the present work we investigate how other shapes can be made, in large quantities. It has been shown before that biaxial stretching of films laden with particles produces disk-like particles.[10,33,34]. The challenge is to produce these in larger quantities. Following Hsiao *et al.*[48] we explored the use of lubricated compression of PMMA laden PDMS films, a method which can easily be scaled up. Preliminary tests with varying the PDMS film diameter and the applied pressure revealed a linear dependency between the applied pressure and the final aspect ratio of the particles and no correlation with the film dimensions. Moreover, the tests showed that with relatively low pressure, 0.36 MPa, it is possible to reach relatively high aspect ratios of 4.3. The PMMA particles synthesised with the stabilisers containing PHSA with short chains (3.6 monomer units) and long chains (15.7 monomer units) subjected to the same amount of pressure (0.1 MPa) using the set-up shown in Figure 2a) were deformed into disk-like particles with aspect ratios 1.6 and 1.5, respectively (Figure 13a) and b)).

Depending on the time of degradation of the PDMS matrix, the PHSA or parts of the PHSA can be cleaved from the particles surface and chemically patterned particles can be produced.[32] The degradation is surface-curvature-dependent, as the flux near regions of higher curvature is higher. Moreover, it can be controlled by the concentration of the degradation agent and the degradation time and facilitates further modification of the

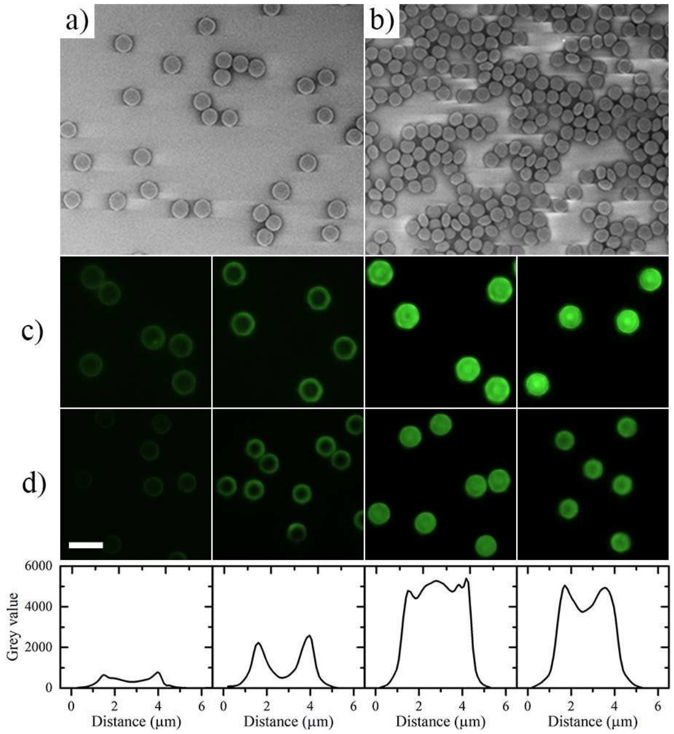

Fig. 13 SEM micrographs of disk-like particles produced by compressing PDMS films laden with PMMA particles stabilised with a) PMMA-*g*-15.7PHSA and b) PMMA-*g*-3.6PHSA. Images in c) and d) correspond to the particles shown in a) and b), respectively, and they show the effects of the degradation time on the stabiliser etching and the subsequent regrafting with a fluorescently. The graphs indicate the progression of the fluorescent area of the particles shown in c). The scale bar represents 5 μm.

anisotropic particles to obtain chemically patterned colloids.[32] The degradation process was quenched at different times and the recovered disk-like particles were re-grafted with a fluorescently labeled stabiliser, to show where the etching had taken place. Initially the degradation occurs at the rim of the particles, and the particles show up as fluroescent circles in the confocal microscope (Figure 13c) and d)). With prolonged degradation times, the regions covered with the labeled PMMA-*g*-PHSA were progressively growing. The length of the PHSA on the surface of the initial spherical particles had no impact on the subsequent grafting after the degradation (Figure 13c) and d)). The same trend was observed with the disk particles produced from the fluorescently labeled spheres. However, in this case, the difference between the re-grafted area and the initial stabiliser is very subtle and it is difficult to observe. The spreading of the fluorescent area over time was quantified by evaluating the grey values of the disks produced from PMMA spheres stabilised with the PMMA-*g*-3.6PHSA (Figure 13).

Uniaxial extension or compression of PDMS films leads to formation of prolate or oblate ellipsoids, i.e. particles with the same dimensions in two directions. However, combining the effects of extension and compression should result in particles with different dimensions in all three directions. In order to achieve this, the set-up used to produce disk-like particles was equipped with channel dies that could be placed between the compressing plates. Since the film width was equivalent to the channel width, the film deformation in the direction of the short axis was constrained, but the compression caused a decrease in sample thickness and an increase in length which resulted in shapes as in Figure 14a) that resemble surfboards (Figure 14b)) due to the triaxial deformation. Such particles may be of interest for studies of interfacial rheology, as there should be no strong lateral capillary forces. The productions of the particles by the lubricated compression can be scaled up to arbitrary quantities and the deformation is rather uniform.

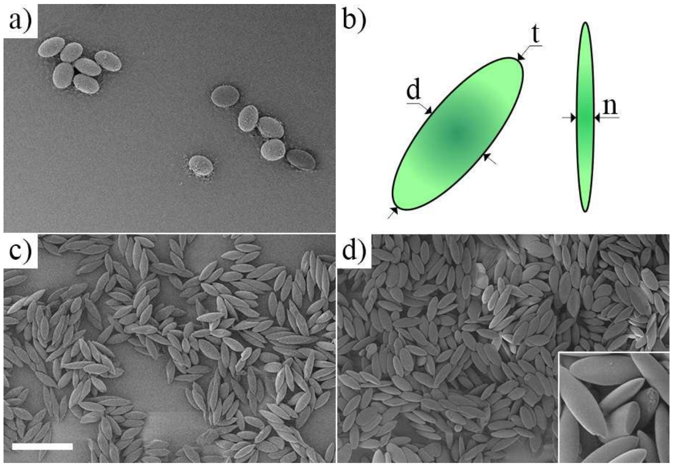

Fig. 14 a) PMMA particles obtained by compressing PDMS films in a channel die. b) A schematic representation of surfboard-like particles. c) and d) PS particles recovered after the biaxial stretching of PVA films. The draw ratios of the films together with the deformation and final aspect ratio of the particles are shown in Table 4 (Experiment a) and b), respectively). The inset in d) shows a close-up on the circumference of the deformed particles. The scale bar indicates 5 μm and the width of the inset image is 3 μm.

For PS particles which need to be embedded in PVA, the squeeze flow method is less suited, due to the different mechanical properties of the PVA. We resorted to plastic drawing of a particle-filled polymer tube over a heated fork (Figure 2a)). The change in shape and diameter between the original tube and the fork sets the deformation of the film and the particles. Some examples of the particles are shown in Figure 14c) and d). The inset in Figure 14d) shows a particle which was broken during processing which nicely shows the cross section. The relation between the draw ratio of the films and the aspect ratio of the particles was investigated for 5 different conditions, and the resulting aspect ratios are given in Table 4. The first two rows correspond to the images in Figure 14c) and d), respectively. Also this method can be scaled up to produce particles in large quantities.

4 Conclusions

The synthesis of model near hard sphere colloids, consisting of PHSA stabilized PMMA colloids, has been revisited. H-NMR spectroscopy was extremely helpful in elucidating the problems which can occur during the polycondensation of the 12-HSA.

Performing the polycondensation in the melt and with a different catalyst as compared to the commonly used ones, enabled a better control over the synthesis of the model near hard spheres. The properties of the particles can be modulated to deviate from near hard sphere behaviour, for example the better control over the synthesis enables us to vary the layer thickness at will. Moreover, we can vary the shape of the particles by mechanical deformation, making prolate or oblate ellipsoids or even triaxial, surfboard-like, particles with methods which apply to different types of latex particles. Finally, using a localised etching, we can make these anisotropically shaped particles also chemically patterned.

5 Acknowledgments

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Table 1 Molecular weights of different 12-PHSA determined by ^{1}H-NMR spectroscopy and gel permeation chromatography.

	NMR		GPC				
Sample	M_n $(r = 1)$/g mol^{-1}	M_n $(r = r_{real})$/g mol^{-1}	M_n/g mol^{-1}	M_w/g mol^{-1}	M_z/g mol^{-1}	M_p/g mol^{-1}	PDI
5.1PHSA	1559	1459	1167	3794	6863	3749	3.3
3.6PHSA	1080	1035	820	2097	3632	1677	2.6
15.7PHSA	6353	4453	5445	10345	15396	10516	1.9
4.9PHSA (75%)	3317	1401	1323	3589	6726	3083	2.7

Table 2 Molecular weights of the different stabilisers.

Sample	M_n (GPC)/g mol^{-1}	M_w (GPC)/g mol^{-1}	M_z (GPC)/g mol^{-1}	M_p (GPC)/g mol^{-1}	PDI
PMMA-*g*-5.1PHSA	6151	29625	59340	25395	4.8
PMMA-*g*-3.6PHSA	28772	79384	193063	47775	2.8
PMMA-*g*-15.7PHSA	8803	23850	55914	14258	2.7

Table 3 Particles diameters determined by SEM and DLS. The hydrodyanmic layer thickness is calculated as differences in the radii determined by the two methods. For comparison, the computed contour lengths of the PHSA are shown and the radii of gyration of the PHSA in solvents of different quality.

	SEM	DLS		Layer	Contour length of	R_g/nm		
Stabiliser	d/µm	d/µm	PDI	thickness/nm	PHSA/nm	Good solvent	θ solvent	Poor solvent
PMMA-*g*-5.1PHSA	1.594±0.042	1.621	0.032	14	7.9	2.7	2.3	1.7
PMMA-*g*-3.6PHSA	1.883±0.028	1.897	0.032	7	5.8	2.2	1.9	1.5
PMMA-*g*-15.7PHSA	2.286±0.054	2.566	0.065	105	22.4	5.2	4.0	2.5

Table 4 The draw ratios of the PVA films laden with PS particles in the transverse, drawing and the direction normal to the stretching direction, particles deformation in the three directions and the final aspect ratios of the recovered particles.

		Film draw ratio			Particles deformation			Particles final
	Temperature/	Transverse /	Drawing /	Normal/	Transverse /	Drawing /	Normal/	aspect ratio/
Experiment	°C	-	-	-	-	-	-	- : - : -
a)	120	2.0	1.0	0.4	2.27	0.78	0.58	4.0 : 1 : 1.4
b)	140	2.3	1.0	0.4	2.40	0.87	0.48	5.0 : 1 : 1.8
c)	140	2.0	0.8	0.6	2.16	0.73	0.65	3.4 : 1 : 1.2
d)	140	3.5	0.6	0.4	4.29	0.68	0.34	12.6 : 1 : 2.0
e)	140	1.3	1.0	0.6	2.32	0.80	0.55	4.3 : 1 : 1.5
f)	140	1.3	1.0	0.5	1.30	0.90	0.85	1.5 : 1 : 1.1