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# Nanogels with High Active β-Cyclodextrin Content as Physical Coating System with Sustained Release Properties

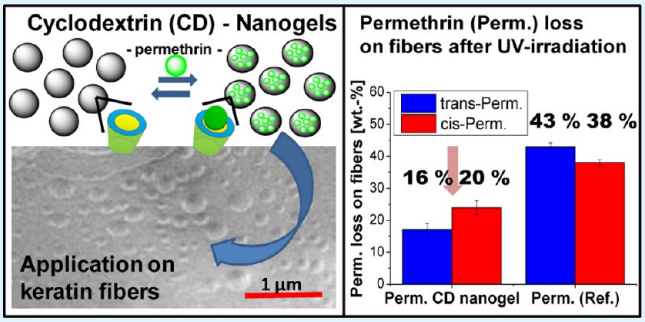
Markus J. Kettel,[†] Karola Schaefer,*[,†] Juergen Groll,[†,‡] and Martin Moeller*[,†]

[†]DWI—Leibniz Institute for Interactive Materials and Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Forckenbeckstr. 50, 52056 Aachen, Germany

[‡]Department and Chair of Functional Materials in Medicine and Dentistry, University of Wuerzburg, Pleicherwall 2, 97070 Wuerzburg, Germany

Supporting Information

**ABSTRACT:** We present the application of nanogels with high functional β-cyclodextrin (β-CD) content as new and versatile method for the modification and protection of textiles. The complexation potential of covalently embedded β-CD in nanogels is demonstrated for the common insecticide permethrin in aqueous environment. It is shown that permethrin containing β-CD nanogels can be applied easily, homogeneously and safely on keratin fibers like wool fabrics and human hairs. The permethrin concentration on fibers is directly controlled by the permethrin content in nanogels. We tested the permanence of permethrin on treated fibers with regard to washing and UV fastness. Our results show that permethrin complexed in nanogels is removed from the textile during washing, but that the complexation of permethrin by β-CD domains in the nanogels protects the active ingredient from UV degradation. Bioassay tests against the larvae of *Tineola bisselliella* and *Anthrenocerus australis* show that the activity of the ingredients does not decrease after complexation in β-CD gels and it results in protection of the wool fibers against degradation by the insect larvae.




**KEYWORDS:** *Nanogels, cyclodextrins, host—guest-systems, permethrin, keratin fibers, textiles*

## 1. INTRODUCTION

Nano- and microgels are small cross-linked polymeric particles, which can be considered as colloidal hydrogels if they are composed of water-soluble/swellable polymer chains. Specific properties like the degree of swelling, particle size or responsibility to changes in the next environment of the nanogels can be controlled by variation of the functional monomers, the degree of cross-linking and the preparation method.[1,2] Furthermore, the embedding of functional molecules with specific binding properties for guest molecules finds more and more interest and application possibilities.[3,4]

For example, incorporation of cyclodextrins (CDs) as specific binding domain into the polymer network promotes improved uptake and release properties of micro- and nanogels and has proven superior to low molecular weight CDs.[5] CDs are well-known for their typical cone structure, which consists of a hydrophilic outer surface and hydrophobic interior cave with a diameter of 5−8 Å. The typical structure properties of CDs enable the formation of host−guest complexes with suitable hydrophobic molecules.[6] Complexation leads to modification of the physical and chemical properties (solubility, smell, reactivity etc.) of the guest molecules.[7] In many fields, CDs find applications as an adsorber and/or switchable release domains.[8,9] Hence, nonbonded natural CDs or covalently bonded modified CDs are already used for encapsulation of bad odors or the fixation and controlled release of perfumes, e.g., in the textile industry.[10,11] CD-containing nanogels have improved properties and advantages compared to low molecular weight CDs. A modified release behavior controlled by copolymerization, an improved fixation on surfaces by physical binding and an improved possibility for specific application might be expected for polymeric CD carrier and delivery systems.[12] Nanogels are known for their ability to adsorb on surfaces and form thin films,[13,14] in which they should conditionally raise fast with a homogeneous distribution onto textiles. On surfaces, nanogels are physically connected due to their gel character. Thus, contrary to covalently bound and nonmodified CDs,[15,16] CD-containing nanogels should be applicable to all types of fabrics and surfaces due to the good adhesion to surfaces caused by the internal cross-linked gel character. The coating of textile surfaces with nanogels has advantages over the application of polymers as it results in very thin and homogeneous gel layers or particles. Polymer application results often in thick and inhomogeneous layers, which has a negative impact on the haptic properties and on the performance of the textiles. The application of conventional polymers, e.g., acrylates, results

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Table 1. Permethrin (perm.) Concentrations in β-CD-sP(EO-*stat*-PO) Nanogel (NG) Dispersions for the Complexation Process[a]

| NG (mg/mL) | calcd CD[b] (mg/mL) | perm. (mg/mL) | calcd CD[b] (μmol/mL) | perm. (μmol/mL) | perm./NG (wt %) | NG/tex. (wt %) | perm./tex. (wt %) |
|---|---|---|---|---|---|---|---|
| 2.99 | 1.50 | 0.00 | 1.32 | 0.00 | 0.00 | 0.38 | 0.00 |
| 2.99 | 1.50 | 0.06 | 1.32 | 0.15 | 2.00 | 0.38 | 0.08 |
| 2.99 | 1.50 | 0.12 | 1.32 | 0.31 | 4.01 | 0.38 | 0.16 |
| 2.99 | 1.50 | 0.30 | 1.32 | 0.77 | 10.02 | 0.38 | 0.39 |
| 2.99 | 1.50 | 0.75 | 1.32 | 1.92 | 25.04 | 0.38 | 0.98 |
| 2.99 | 1.50 | 1.50 | 1.32 | 3.83 | 50.09 | 0.38 | 1.94 |

[a]For quantitative analysis of the permethrin content on treated fibers, the percentage weight ratio of permethrin and wool textile (tex.) (3.79 g ≈ 200 $cm^2$) is shown. [b]Calcd CD: calculated β-CD content in β-CD nanogels based on an expected conversion of 1:1 ratio β-CD: NCO-sP(EO-*stat*-PO).

often in textiles with stiff handle.[17,18] The ability to form stable nanogel dispersions in water is a further major advantage over polymers that are often applied from organic solvents. Thus, loaded and unloaded CD nanogels can be applied on different surfaces from aqueous dispersion. This process enables an easy handling and a safe and nontoxic application process. Furthermore, physically bonded nanogels loaded with specific ingredients should also be removable and exchangeable.

One major interest for textiles is the protection of human beings, animals, and the textile material itself against insect attack. Permethrin (3-phenoxybenzyl (1*RS*)-*cis*,*trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate), which belongs to the synthetic pyrethroids, is one commonly used agent and has applications as a common insecticide, acaricide, and repellent agent with a broad range in its activity spectra.[19−21] It acts as a neurotoxin and is responsible for prolongation of the sodium channel activation. The unimpeded flow of $Na^+$ ions through the cell membranes leads to uncontrolled nerve impulses, incoordination and finally paralysis of the organism.[22,23] Permethrin is used in agriculture to protect plants and to kill livestock parasites.[24,25] Furthermore, it is effective for the industrial domestic insect control. As an insect repellent, it has applications against ticks and mosquitoes and use in pet flea preventative collars.[26,27] As a personal protective, permethrin is used as a repellent in cloth impregnation and has applications primarily for the treatment of military uniforms and mosquito nets.[28] In medicine, permethrin is a first-line treatment for scabies and is used on humans to eradicate parasites such as head lice and mites.[29−31]

The complexation of insecticides and, especially, of permethrin by β-CD is well studied by different workgroups.[32−34] Experimental studies in cooperation with theoretical calculations show that in low β-CD concentrations, a 1:1 complex is formed and, in higher concentrations, a 1:2 complex is formed. The complexes are ordered in nanorods when the surplus of β-CD and thus, the complex density of 1:2 increases.[35] Also, the application of permethrin:β-CD complexes onto textiles, especially on cotton and polyester fabrics,[36−38] or their incorporation in mosquito nets has been investigated.[39] The results show that the activity of the agent is not reduced by complexation but it is observed that β-CD, which possesses high biocompability, enhances the activity.

However, the use of β-CD-containing nanogels for complexation of permethrin and as a protective coating for textiles has not yet been explored. Coating possibilities with permethrin complexed by β-CD-containing nanogels for different fiber types offer a new application method for insecticides, aiming further at the protection of textiles against the attack of the larvae of moths or beetles or to protect humans against mosquitoes and head lice. The active agent is released during contact or attack of insects on the fabrics; therefore, it acts as a stomach or contact poison. Rapid, uncontrolled release and early decomposition of the active agents on the fabric should be prevented by the complexation in β-CD domains.[40]

We have shown before that by the use of reactive multifunctional prepolymers, β-CD can be cross-linked in a water-based organic solvent-free approach to nanogels with up to 60 wt % active β-CD content.[41] The aim of the present work is the complexation of permethrin as a model insecticide into these nanogels and their use for coating textiles for protection against insects. Studies regarding the permethrin uptake, coating on keratin fibers and the permanence of the treated textiles are presented and discussed. Furthermore, the activity of the permethrin β-CD nanogel treated keratin fabric is tested in bioassays against the larvae of *Tineola bisselliella* (clothes moth) and *Anthrenocerus australis* (carpet beetle).

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** β-CD was obtained from Wacker GmbH, Burghausen, Germany, and dried before use at 80 °C for about 48 h in a drying cabinet. Isocyanate-terminated star-shaped poly(ethylene oxide-*stat*-propylene oxide) (NCO-sP(EO-*stat*-PO)) was prepared as described before.[42] Here, star-shaped polyethers with a backbone of statistically copolymerized 80% ethylene oxide and 20% propylene oxide have a molecular weight of 12 000 g/mol (PDI = 1.15) and are terminated with isocyanate (NCO) groups at the distal ends of the arms. Both *trans*- and *cis*-permethrin were obtained from Sigma Aldrich, Taufkirchen, Germany, and used as received. A mixture of *trans*- and *cis*-permethrin with the common ratio of 75% (trans) to 25% (cis), which are used for standard treatment of wool textiles, was diluted in minimum of methanol. The used wool fabrics (179.35 g/$m^2$, tissue thickness: 0.845 mm; raw white) was provided by Becker & Fuehren Tuche GmbH, Aachen, Germany. The used human hair (European hair type) was received from the author.

**2.2. Preparation of β-CD-Containing Nanogels.** β-CD-containing nanogels were synthesized according to the published preparation procedure.[41,42] 502 mg (0.44 mmol) of β-CD were dried at 80 °C for about 48 h and dissolved in deionized water (50 mL). The aqueous β-CD solution was added to 504 mg (0.028 mmol) of the NCO terminated sP(EO-*stat*-PO) prepolymer under stirring. The aqueous phase was stirred continually at 300 rpm over 24 h using a glass paddle connected to an overhead stirrer. The clear dispersion was filled in a dialysis tube (ZelluTrans -12,0S 45 mm, MWCO: Nominal 12 000−14 000; Carl Roth GmbH, Karlsruhe, Germany), which was put into water (2 L). The water was changed after 24 and 48 h, and the dialysis was stopped after 96 h. The purified dispersion was filled up to a 250 mL end volume. Yield: 748.7 mg (74%). Particle size: 50−200 nm. Further analytical data are given in the Supporting Information.

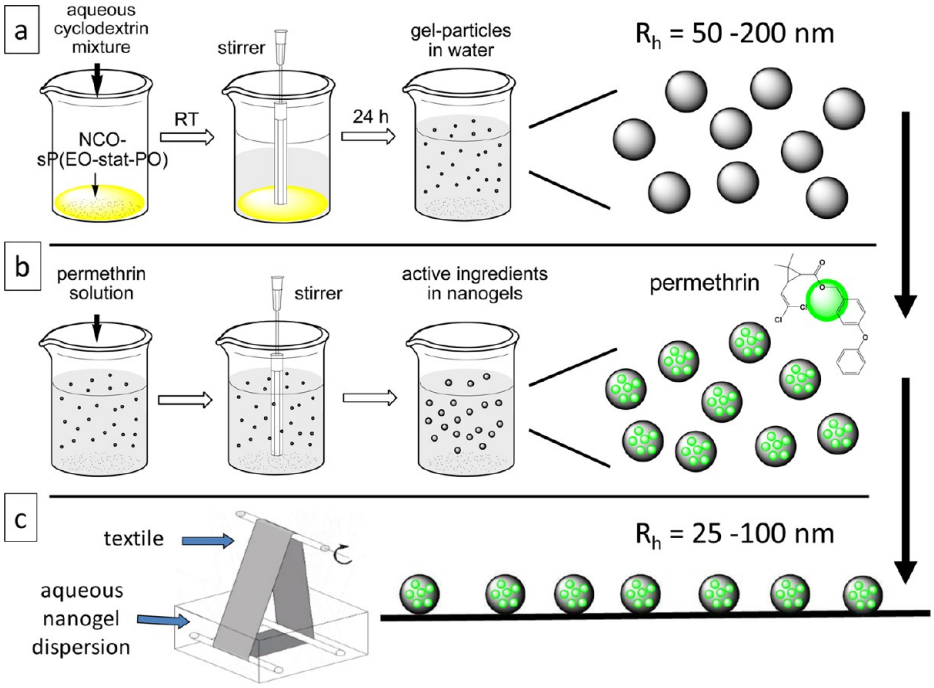
**2.3. Complexation of Permethrin by Nanogels.** *trans*- (75%) and *cis*- (25%) permethrin containing methanolic solutions were added in different concentrations to a 50 mL aqueous β-CD-containing nanogel dispersion (3 mg/mL). The reaction mixtures were stirred for 12 h at room temperature (RT) for full complexation and

Table 2. $\beta$-CD-sP(EO-*stat*-PO) Nanogel (NG) and Permethrin (perm.) Concentrations of Aqueous Dispersion for the Coating by Padding with the Help of a Mini-Foulard Plus the Percentage Weight Ratio of Permethrin and Wool Textile (tex.) (3.79 g ≈ 200 cm$^2$)

| NG (mg/mL) | calcd CD[a] (mg/mL) | perm. (mg/mL) | calcd CD[a] ($\mu$mol/mL) | perm. ($\mu$mol/mL) | perm./NG (wt %) | NG/tex. (wt %) | perm./tex. (wt %) |
|---|---|---|---|---|---|---|---|
| 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 0.60 | 0.30 | 0.06 | 0.26 | 0.15 | 10.02 | 0.78 | 0.08 |
| 1.50 | 0.75 | 0.15 | 0.66 | 0.38 | 10.02 | 1.94 | 0.20 |
| 2.99 | 1.50 | 0.30 | 1.32 | 0.77 | 10.02 | 3.80 | 0.39 |
| 12.00 | 6.00 | 1.20 | 5.29 | 3.07 | 10.02 | 13.67 | 1.56 |

[a]Calcd CD: calculated $\beta$-CD content in $\beta$-CD nanogel based on an expected conversion of 1:1 ratio $\beta$-CD: NCO-sP(EO-*stat*-PO).

Scheme 1. Synthesis of $\beta$-CD-Containing Nanogels Based on NCO-star P(EO-*stat*-PO) in Aqueous Solution (a), Incorporation of Permethrin into $\beta$-CD-Containing Nanogels in Aqueous Solution (b) and Nanogel Application on Textile Surfaces (c)




evaporation of the methanolic solvent. After a few minutes, white, cloudy, stable particle dispersion was formed. The stable dispersions are separated from noncomplexed permethrin sediments and freeze-dried or applied directly onto keratin fibers for further analysis. Table 1 shows the total permethrin concentrations in the $\beta$-CD nanogel dispersion for the complexation process. The added molar permethrin concentration was calculated for the expected molar $\beta$-CD content in nanogels by theoretical conversion of a 1:1 ratio of $\beta$-CD and NCO-sP(EO-*stat*-PO). Further analytical data are given in the Supporting Information.

**2.4. Application of Permethrin Loaded Nanogels onto Textiles.** A series of nanogel dispersions with different particle and permethrin concentrations was used for further coating experiments. The quantitative permethrin application with the associated nanogel concentration on textiles is shown in Table 1. The nanogel concentrations and the associated permethrin content used for different coatings are listed in Table 2. The coating process took place in a special beaker into which the dispersion was placed. The wool textiles (3.79 g ≈ 200 cm$^2$) were padded with 50 mL of a dispersion containing permethrin loaded nanogel particles for 30 min using a mini-foulard (in-house development) (Scheme 1c). After that, the coated fabric was dried at RT for 30 min and further for 30 min at 80 °C. The tissue samples were packed waterproof and stored under ambient conditions protected from light.

**2.5. Application of Permethrin-Based Insecticide onto Wool Textiles (Reference Treatment).** Permethrin-based insecticides (here: Eulan SPA-01, Tanatex GmbH, Leverkusen, Germany, and Mystox CMP, Catomance Technologies Ltd., Stevenage, United Kingdom) were applied onto wool fibers or fabrics in dosages of 0.3–1.0% (wt % on weight of wool) from an aqueous liquor (liquor ratio = 1:30) that contained 4% (wt % on weight of wool) $(NH_4)_2SO_4$, the pH value was adjusted to 6 using acetic acid by a bath exhaustion procedure. The treatment was performed at 98 °C for 60 min using an Ahiba Turbomat (Type TM6) laboratory dyeing machine (Ahiba, Birsfelden, Switzerland). The wool samples were rinsed after the treatment with warm water (50 °C) for 10 min and with cold tap water for 20 min. The samples were squeezed off and dried at ambient conditions protected from light exposure. In parallel, blank treatments without addition of insecticides were performed.

**2.6. Characterization of $\beta$-CD-Containing Nanogels, Permethrin Loaded Nanogels and Keratin Fibers and Fabrics Treated with Permethrin.** IR spectra were obtained using a Nexus 470 FT-IR spectrometer (Thermo Nicolet, Neu-Isenburg, Germany) (spectral disintegration: 8 cm$^{-1}$). Nanogel dispersions were dried by lyophilization and studied preferentially in KBr pellets. Raman spectra were measured with a spectral resolution of 4 cm$^{-1}$ with the help of a Bruker RFS 100/s Raman spectrometer (Bruker Optics, Ettlingen, Germany) using a Nd:YAG laser (wavelength: 1064 nm). The solid samples were measured in an aluminum pan.

$^1$H and $^{13}$C NMR measurements were carried out using a AC400 spectrometer (Bruker, Ettlingen, Germany); $^1$H NMR spectra were recorded at 400 MHz and $^{13}$C NMR spectra at 100 MHz. DMSO-$d_6$ was used as solvent; the signal of the nondeuterated solvent was used as standard.

UV−vis spectra were measured with the help of a Varian Cary 100 UV−vis spectrophotometer (Varian, Darmstadt, Germany) using quartz cuvettes (optical path length: 1 cm). The respective solvent (here: water or ethanol) was used as a reference.

Analysis of the particle size was made by dynamic light scattering measurements (DLS) using a Nano Zetasizer (Malvern Instruments GmbH, Herrenberg, Germany) spectrometer. The spectrometer contains a He−Ne laser ($\lambda_0$ = 633 nm). Back scattering light was detected using an angle of 173°. The hydrodynamic particle radius and the particle distribution of the hydrodynamic radius were determined. All DLS measurements were made at 25 °C.

The electron microscopic analyses were made using the S-4800 field emission scanning electron microscope (Hitachi Ltd., Tokyo, Japan) with high disintegration and cryofunction.

Dry nanogels were studied after coating onto the surface of keratin fibers. After application of nanogels by padding or dip-coating, the treated fibers were dried further at RT and in vacuum. The samples coated with nanogels were studied by scanning electron microscopy (SEM) at RT using an accelerating voltage of 1 KV and 8 mm disintegration. The particle diameter was determined with the help of the SEM enclosed software.

The permethrin concentration of $\beta$-CD-based nanogels was determined by RP-HPLC analysis with the help of Nucleosil 100-5 $C_{18}$ columns (Macherey & Nagel GmbH, Dueren, Germany) using the eluent methanol/water 87/13 (v/v), and a flow rate of 0.5 mL/min at RT. The exact concentration was determined by the use of UV detection at 206 nm and a straight calibration line of pure permethrin. The permethrin content of treated textiles and of freeze-dried nanogels was determined by HPLC analysis after extraction with methanol (1 g textile/20 mL methanol; 30 min at 80 °C).

The fastness to washing of treated textiles was determined according to DIN EN ISO 105-C10 at 40 °C (30 min). Five grams of needle soap was used for the washing of 1 g of wool in 50 mL of soap solution. The textile was then further washed with water for 10 min and 2 times with distilled water.

The evaluation of the insecticide resistance to washing was performed by determination of the residual content of the parasite protection products after washing fastness tests by HPLC analysis after extraction of the wool.

The light fastness testing of treated fabrics was performed according to DIN EN ISO 105-B06. Here, permethrin treated fabrics were irradiated for 48 h in an Atlas Weather-Ometer ES25 instrument (ATLAS Material Testing Technology, Chicago, USA) at a light intensity of 0.27 W/m$^2$/nm (recorded at 340 nm). The evaluation of the insecticide resistance to light was performed by determination of the residual content of the parasite protection products on treated wool after the light fastness test by HPLC analysis after extraction of the textile.

The color measurement was performed using a Datacolor Spectraflash SF600 plus CT colorimeter from Datacolor, Marl, Germany. The measurements were made without luster and with a 20 mm blend. They were performed using illuminant D65 and the 10° observer. Fabrics were measured in two layers. For each sample, five measurements were made and the mean values were calculated. The whiteness was calculated as W-CIE, the yellowness values as G-DIN 6167 and the yellowness differences as ΔG-DIN 6167. The color values were calculated according to the Datacolor formula based on the CIELAB system and for illuminant D65.

The biological activity of wool fabrics coated with permethrin containing nanogels was determined according to ISO 3998-1977 (E) (in accordance with the Wools of New Zealand Test Method 25) against the larvae of moths (*Tineola bisselliella*) and against the larvae of the Australian carpet beetle (*Anthrenocerus australis*) at AgResearch, Inc., Hamilton, New Zealand.

## 3. RESULTS AND DISCUSSION

The aim of this work was to evaluate and exploit the application potential of nanogels as surface-active carriers and anti-insect coatings for textiles. For this, nanogels were chosen to act as carrier materials for permethrin as a model compound with regard to fixation and as coating systems due to self-bonding on fiber materials. The whole application procedure is subdivided into three main steps (Scheme 1a−c).

Preparation and purification of nanogels with high active $\beta$-CD content is followed by complexation of permethrin into the nanogels. Finally, the treatment of fabrics by coating with the loaded nanogels from washing liquors and thermofixation of the treated materials was performed, and their bioactivity was tested.

**3.1. Cyclodextrin Based Nanogels.** Nanogels are prepared in water by the cross-linking of $\beta$-CD with a NCO-terminated star-shaped prepolymer on the basis of polyethylene oxide (80%) and polypropylene oxide (20%) (sP(EO-*stat*-PO)) as described before.[41,42] The colloidal polymeric particles are created and stabilized by incorporation of $\beta$-CD domains in the polymer backbone of cross-linked sP(EO-*stat*-PO) in aqueous solution via covalent urethane bonding between the NCO groups of the prepolymer and the hydroxy groups of the $\beta$-CD units.[41] Furthermore, their size of several nanometers can be controlled by the $\beta$-CD content, as an increasing $\beta$-CD concentration in the reaction mixture leads to an increase of the size from 50 nm to several hundred nanometers. We investigated before the uptake capacity of these nanogels and quantitatively determined the complexation properties of the $\beta$-CD units in the nanoparticles by the dye−sorption method using the pH sensitive dye phenolphthalein.

For the present study, we initially checked whether these nanogels do attach onto keratin fibers when applied from aqueous dispersion (Figure 1: nanogel adsorption on wool fibers).

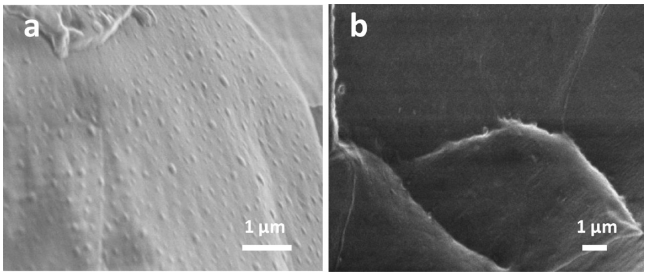
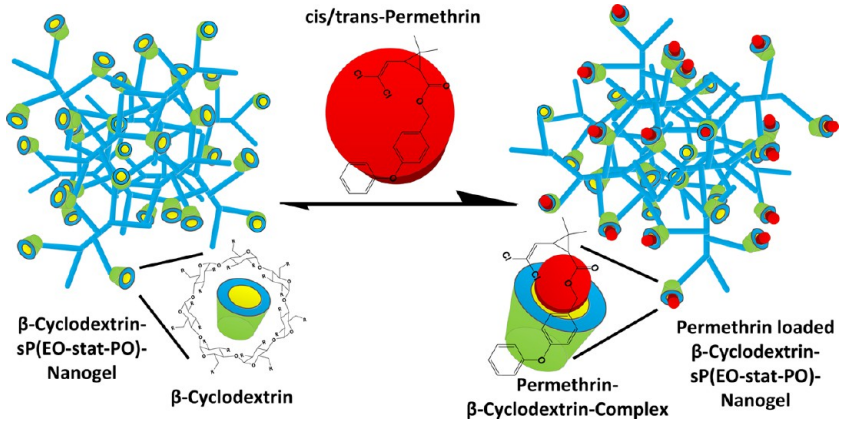



**Figure 1.** $\beta$-CD nanogels coated on wool fibers (a) and uncoated wool fibers as reference (b).

The $\beta$-CD-containing nanogels can be coated onto fabrics by padding, resulting in a highly homogeneous distribution, as analyzed by field emission electron microscopy (FESEM). Only FESEM with a high resolution enables the optical detection of the applied nanogels. After application, the homogeneous coating of the wool fabrics with unloaded gel particles with a size of approximately 100 nm (hydrodynamic radii ($R_h \approx 50$ nm)) is determined.

**3.2. Complexation and Release of Permethrin by/from CD Nanogels.** Complexation of permethrin by natural low molecular weight CDs has already been studied in detail by some workgroups. Stoichiometric formation of a 1:1 permethrin:$\beta$-CD complex is described using higher permethrin concentration and lower $\beta$-CD content in aqueous solution. By increases of the $\beta$-CD ratio, in comparison to permethrin, the formation of a 2:1 complex and the formation of nanorods was described.[32,33]

**Scheme 2. Uptake and Complexation Process of *cis*/*trans*-Permethrin in *β*-CD-Containing Star P(EO-*stat*-PO) Nanogels in Aqueous Dispersion**




In this work, the complexation of permethrin by *β*-CD nanogels is made in aqueous dispersion (Scheme 2). Different concentrations of permethrin diluted in alcohol solutions were added dropwise to *β*-CD-containing nanogels in a clear aqueous dispersion. The complexation of the hydrophobic molecule is observed directly from the decrease of transparency. Hence, hydrophobic molecules bind to the hydrophobic interior surfaces of covalently embedded *β*-CD, which makes nanogels more hydrophobic. The water insoluble ingredients increase their water solubility by complexation and are distributed homogeneously in the whole dispersion (Supporting Information, Figure S1).

The qualitative uptake of permethrin by CD nanogels was studied by IR, Raman, UV and NMR spectroscopy of the freeze-dried permethrin loaded CD nanogels (Figures 2 and S2 (Supporting Information)).

Infrared spectroscopy shows, besides the characteristic bands of the stretching vibration of C−O−C bonds associated with *β*-CD (1030 $cm^{-1}$), the typical amide bands (1677 and 1535 $cm^{-1}$) and the urethane amide I band (1720 $cm^{-1}$), which confirm the chemical cross-linking and the covalent bonding of *β*-CD into the sP(EO-*stat*-PO) based nanogels. The complexation of permethrin is documented by the IR bands at 1585, 1487 and 1457 $cm^{-1}$, which can be assigned to aromatic residues. The C═O band of the permethrin ester groups at 1728 $cm^{-1}$ (*trans*-permethrin) and 1718 (*cis*-permethrin) is overlapped by the amide band at 1720 $cm^{-1}$ of the urethane groups in the nanogel (Figure 2a). In the *β*-CD nanogel:permethrin complex, the vibration of the C═O bond is found at 1720 $cm^{-1}$. In the literature, Shao et al. studied the complexation of permethrin by natural CD using IR spectroscopy and proved that the characteristic peaks of permethrin and CD are not changed by forming an inclusion complex.[43] The results are in agreement with our results, which do not show any significant change of the characteristic IR bands.

In Figure 2b, the region of the Raman spectra between 1020 and 980 $cm^{-1}$ is shown. The Raman signal at 1003 $cm^{-1}$ originates from breath vibrations of the aromatic rings of noncomplexed permethrin. After complexation of permethrin by *β*-CD or by CD nanogels, the breath vibrations of the benzene rings were recorded as sharp Raman peak at 1000 $cm^{-1}$. The shift to lower wavenumbers documents the inclusion of permethrin in the *β*-CD cavity. Wei et al. described also a shift of the breath vibration in the Raman spectrum from 1003 $cm^{-1}$ to 999 $cm^{-1}$ after inclusion of permethrin by *β*-CDcyclodextrin.[44] This result led the authors to the conclusion that the phenyl moiety of permethrin is included inside the cavity of *β*-CD.[44] Furthermore, the Raman bands at 1595, 1617, 1732 and 3055 $cm^{-1}$ can be referred to the complexed permethrin as these signals are due to the C—C−, C═C− (olefinic or aromatic), ester and C—H (aliphatic and aromatic) residues in the permethrin molecule (Supporting Information, Figure S2b). The successful incorporation of *β*-CDs into sP(EO-*stat*-PO) gels is proven by the presence of the out-of-plane deformation of the glucose ring at 480 $cm^{-1}$ in the Raman spectrum (Supporting Information, Figure S2b).

The UV spectra of *β*-CD nanogels, which are loaded with permethrin, exhibit a characteristic UV maximum at 278 nm which originates from the aromatic residues of the permethrin molecule (Figure 2c). The complexation of permethrin by natural *β*-CD and *β*-CD nanogel resulted in a slight red shift of the UV absorption band compared to that of permethrin (273 nm). This effect can be explained by the high electron density of the permethrin guest molecule located inside the *β*-CD host cavity.[25] In the literature, Yang et al. proved the inclusion complexation of permethrin by *β*-CD using UV spectroscopy. They characterized also a slight red shift after inclusion complexation of permethrin by natural CD.[33] In our studies, we compared free permethrin and the inclusion permethrin:*β*-CD complex with permethrin complexed by *β*-CD-containing nanogels. Our results are in agreement with Yang's results.

The $^1H$ NMR spectra in Figure S2d (Supporting Information) of *β*-CD nanogels with complexed permethrin depict the characteristic peaks of the sP(EO-*stat*-PO) backbone at 1.04 ppm and 3.35 ppm, which is overlapped by the CH and $CH_2$ protons of the CD ring in the area of 3.2−3.6 ppm. Furthermore, CD shows the characteristic peak at 4.83 (s, CH-1) and the peaks of the OH groups at 4.53 (s, C—OH-6) and 5.62−5.66 (s, C—OH-2, 3). The complexed permethrin in the nanogel is depicted at $^1H$ NMR signals at 1.164 and 1.210 ppm ($CH_3$, permethrin), 1.989 and 2.065 ppm (C—H, cyclopropane, permethrin), 5.100 ppm (COO—$CH_2$—Ar), 6.045 and 6.250 ppm (cis/trans HC═$CCl_2$), and 6.971, 6.985, 7.026, 7.143, and 7.403 ppm ($CH_{ar}$) (Figure S2d).

In more detail, the spectra in Figure 3a show the region from 6.90−7.05 ppm. The signals characterize five protons of the aromatic rings of the guest molecule permethrin. A downfield shift from 7.004 to 6.985 ppm in the case of the complexed permethrin, in comparison to noncomplexed permethrin, is detectable for two aromatic protons, which should be placed in

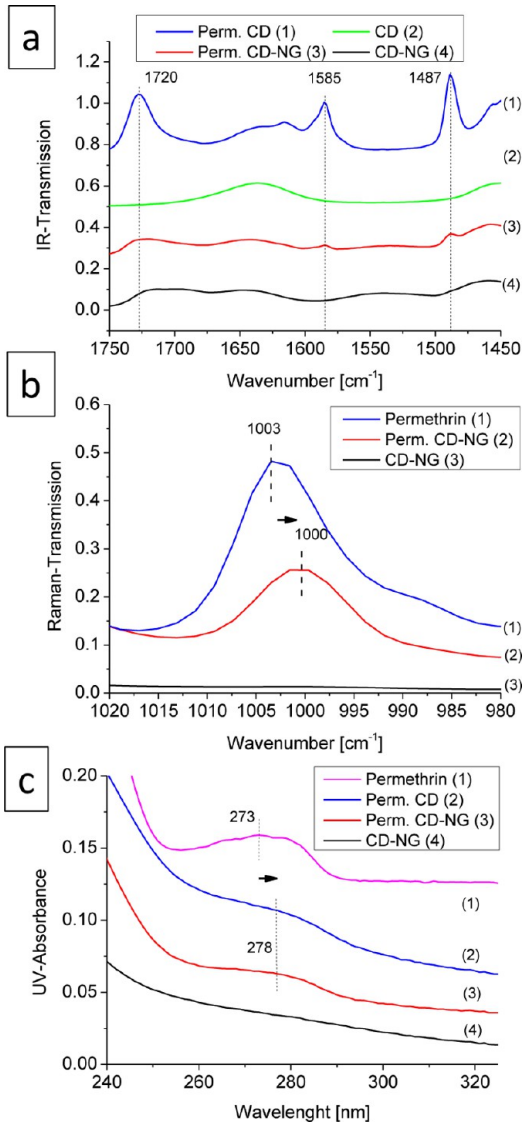



**Figure 2.** IR spectra of $\beta$-CD and the permethrin:$\beta$-CD inclusion complex (Perm. CD) in comparison with $\beta$-CD nanogels (CD-NG) and permethrin loaded nanogels (Perm. CD-NG) (a). Raman spectra of permethrin, permethrin loaded (Perm. CD-NG) and unloaded $\beta$-CD nanogels (CD-NG) (b). UV absorption spectra of permethrin in ethanol and the permethrin:$\beta$-CD inclusion complex (Perm. CD) in water in comparison with $\beta$-CD nanogels (CD-NG) and permethrin loaded nanogels (Perm. CD-NG) in aqueous dispersion (c).

the middle of the CD ring. This downfield shift is similar to the proton shift induced from natural CD on the guest molecule. Hence, it shows that the middle aromatic ring is shielded by the CD molecule. Furthermore, in Figure 3b, the two C−H units of the cyclopropane ring also depict a typical downfield shift after complexation in CD, which also occurs due to interaction of these protons with the CD ring. Both *cis*- and *trans*-permethrin, which are used for the complexation studies, are characterized by the HC═$CCl_2$ proton at 6.045 ppm (trans) and 6.250 (cis) ppm in the spectra in Figure 3c,d. Here, interaction of the HC═$CCl_2$ unit of permethrin with one proton depicts a downfield shift in the case of the permethrin complex with natural CD and bonded CD in nanogels. Furthermore, weak shifts of CD proton peaks are detectable in the range of 3.00−4.00 ppm. In comparison to unloaded CD domains, the weak shifts are induced by host−guest interaction with the CD cavity and permethrin. The results show that all detected peak shifts in the $^1$H NMR spectra of permethrin loaded by CD nanogels explained by changes in the microenvironment of the guest molecule are similar to the proton shifts induced by complexation of permethrin in natural CDs. Thus, we conclude that permethrin is complexed and shielded by the CD units in the nanogel structure.

From all the data of the spectrometric analysis and, in comparison with pure *cis*/*trans*-permethrin, the permethrin cyclodextrin complex and the unloaded CD nanogel, it can be concluded that permethrin is complexed mainly by the CD domains in the nanogels. Furthermore, it is difficult to analyze how much permethrin is complexed by the CD units with this analytical methods and otherwise, how much is encapsulated by the cross-linked structure of the sP(EO-*stat*-PO) polymer backbone. In this case, synergistic effects between the CD domains and the polymer enhance the uptake process.

In water, the CD nanogel complex is quite stable because the hydrophobic guest molecule prefers the hydrophobic interior cavity of $\beta$-CD molecules. By use of organic/water mixtures permethrin release is expected due to the redispersion of the CD nanogels in water. Hence, $\beta$-CD nanogels (2.99 mg/mL) with included permethrin are tested for their release behavior in methanolic solutions. Here, the freeze-dried permethrin loaded nanogels are extracted by methanolic solvent (150 mg/20 mL) and are washed by variation of time at 80 °C under permanent shaking of the mixture. Then, the methanolic extraction solution is filtered and analyzed by HPLC analysis, to determine the permethrin content quantitatively similar to the literature.[45,46]

In Figure 4a, the HPLC diagrams of permethrin released from nanogels in comparison to unloaded nanogels in methanol are shown. The $\beta$-CD nanogels without permethrin do not show any significant peaks. This means that only released permethrin is detected at 206 nm. The permethrin loaded nanogels release the guest molecule, and in the HPLC diagrams, *cis*- and *trans*-permethrin can be detected by the strong peaks at 17 min (trans) and at 21 min (cis) in a ratio of 75% (trans) to 25% (cis). This ratio of the cis/trans isomers is similar to the ratio (3/1 trans/cis) of the original permethrin solution, which is added to the $\beta$-CD nanogel dispersion. Thus, the $\beta$-CD nanogel complex releases *trans*- and *cis*-permethrin without any preference of one of the isomers.

In Figure 4b, the variation of the methanol/water content in the extraction solvent and the extraction time are studied. Here, a mixture of water and methanol (1:1) shows a slight release of permethrin from $\beta$-CD nanogels. Change of extraction time does not lead to an increase of the released permethrin content. On the opposite, the pure methanolic solution increases the release of *trans*- and *cis*-permethin significantly. Here, the extraction time can promote the released amount of *trans*- and *cis*-permethrin. The total content of the complexed permethrin is rinsed out by pure methanol. The hydrophobic properties of the guest molecule in a less hydrophilic environment plus the high hydrodynamic pressure due to the surplus of the solvent lead to a rising release of permethrin in organic solvents. The concentration of the released permethrin in pure methanol increases to 100% of the expected values. These values are 90% higher than the permethrin release in a water/methanol mixture (1:1).

**3.3. Application onto Keratin Fiber Materials.** Stable aqueous nanogel dispersions loaded with permethrin suggest a good possibility for the application on surfaces. The treatment

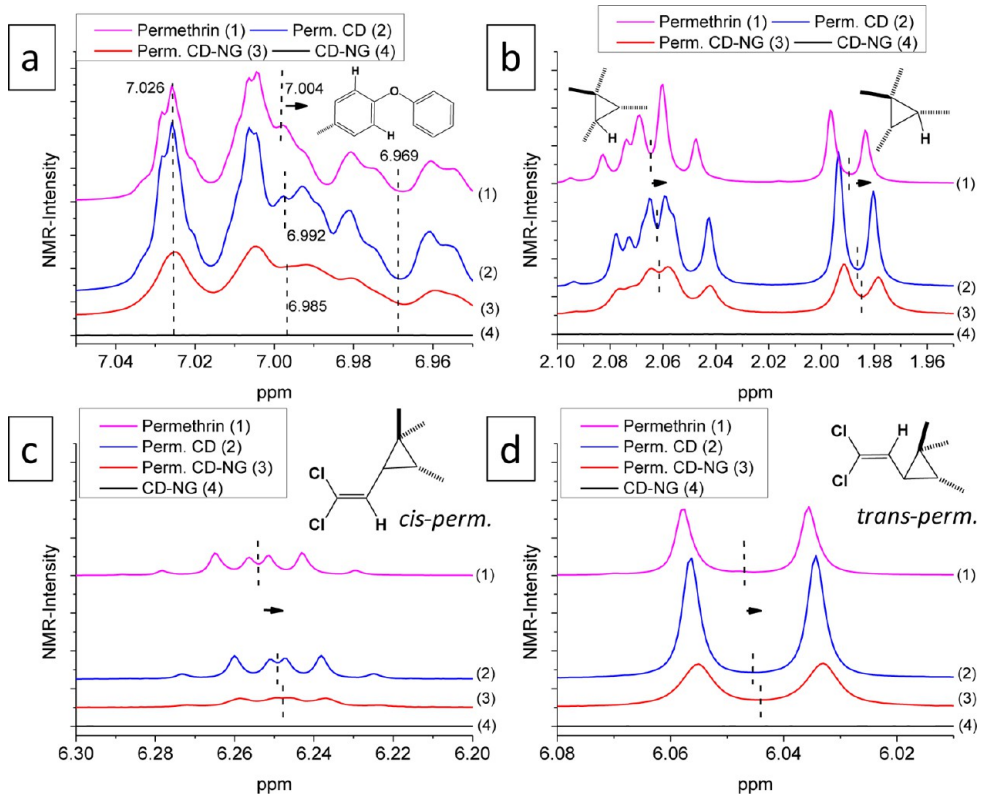



**Figure 3.** Special regions of the $^1$H-NMR spectra of cis/trans-permethrin and the cis/trans-permethrin:$\beta$-CD inclusion complex (Perm. CD) in comparison with $\beta$-CD nanogels (CD-NG) and cis/trans-permethrin loaded nanogels (Perm. CD-NG) in DMSO-$d_6$ (d).

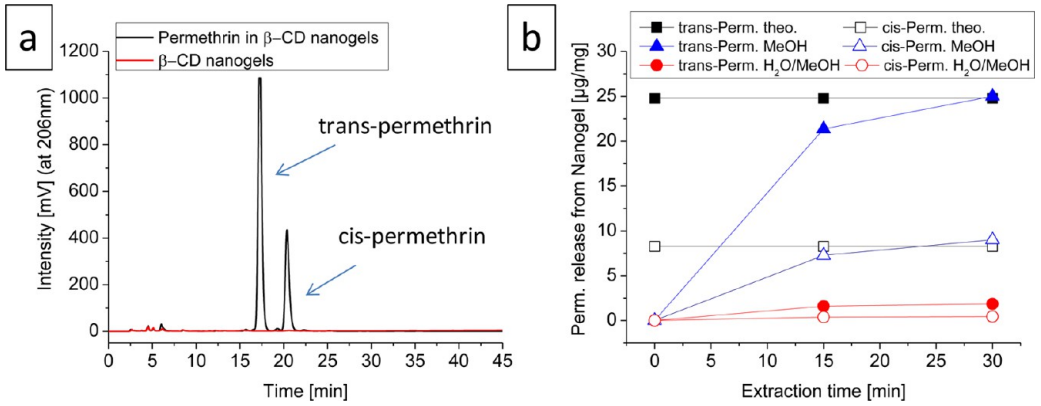



**Figure 4.** Release of permethrin (Perm.) from $\beta$-CD nanogels in methanolic solutions determined by HPLC analysis. HPLC diagram of *trans*- and *cis*-permethrin released from loaded $\beta$-CD nanogels in comparison with unloaded $\beta$-CD nanogels in methanol (a). *trans*- and *cis*-permethrin release from $\beta$-CD nanogels by variation of the methanol/water content of the extraction solvent and variation of extraction time (b).

of textiles, especially of wool fabrics, with permethrin loaded nanogels presents a controlled, but effective, insect proofing with safe applications. The coating process is made by dip-coating and padding. Keratin fibers like wool or human hairs can be treated easily with permethrin from aqueous liquors. The coatings are studied using aqueous dispersions with different $\beta$-CD nanogel concentrations (Table 1). The surface of wool fabrics, which were treated with permethrin loaded $\beta$-CD-containing nanogels, is analyzed by field emission electron microscopy (Figure 5). Slightly coated fabrics are obtained by padding using 0.6 mg/mL (0.8 wt % permethrin/textile) permethrin loaded nanogel dispersion (Figure 5b). In comparison to the untreated fabric (Figure 5a), the surface shows the presence of small round particles. The particle concentration, and thus, the permethrin concentration on fibers increase with the increase of the permethrin loaded particle concentration in the aqueous dispersion (Figure 5b–d). An increase of the nanogel concentration to 1.5 mg/mL (2 wt %) results in a higher particle concentration on the surface. Heavily coated fibers, which can be seen in Figure 5d, are obtained with nanogel concentration of 3 mg/mL (4 wt %). Here, agglomerations and dense distribution characterize the surface of the fabric. Very heavily coated fabrics obtained by using nanogel concentrations of 12 mg/mL (16 wt %), exhibit the presence of a gel film, which adheres to the fabric and cross-links the individual wool fibers (Figure 5e). In case of coatings with low nanogel concentrations, individual gel particles can be identified with relatively homogeneous distribution on the wool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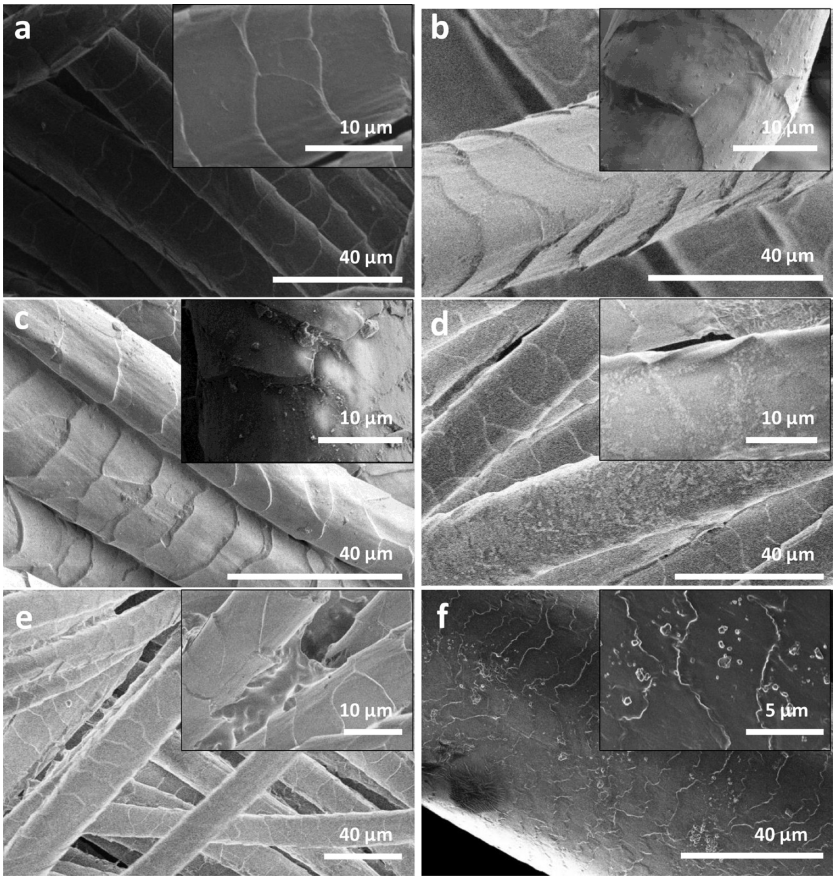


**Figure 5.** FESEM images: uncoated (a), slightly coated with clearly identifiable permethrin loaded $\beta$-CD nanogels on wool fibers (b–f) and heavily coated wool fibers (e). Panel f shows permethrin loaded nanogels applied onto human hairs. (FESEM images of untreated human hairs are given in the Supporting Information as Figure S3).

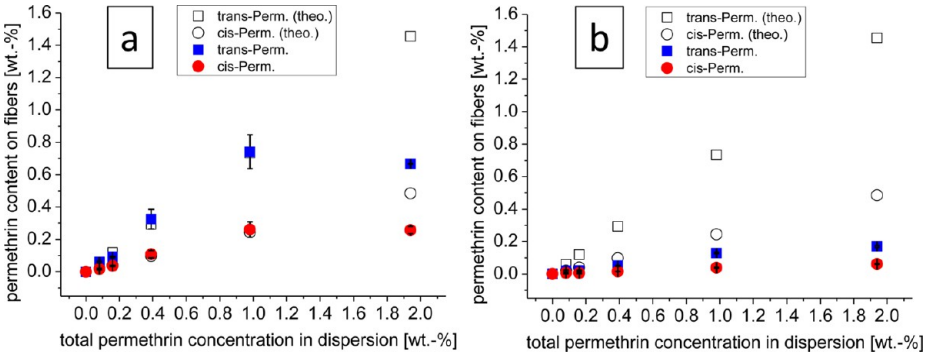


**Figure 6.** Quantitative determination of the permethrin content of CD gel particles obtained by extraction of treated wool fabrics with methanol and detection at 206 nm using HPLC analysis in dependence on the applied permethrin concentration (= theo.) of the CD nanogel dispersion. Measurements after treatment (a) and determination of the permethrin amount after 3 years of storage (b).

fibers. At high resolution, the particles show a homogeneous distribution with dimensions of 100 to 200 nm. The nanogels are difficult to detect at low resolution. The morphology of the particles on the surface can be described as spherical.

In Figure 5f, human hairs, which are treated with permethrin containing nanogels by dip-coating, are shown. Here, a low concentrated nanogel dispersion was used, which results in slight coating with particles. The treatment of human hairs with permethrin containing CD nanogels might be a possible application against head lice. Permethrin loaded nanogels can be used in shampoos or water based conditioners. The fixation of permethrin by nanogels on hairs exhibits long activity and minimizes skin irritations caused by a reduction of application repetitions and uncontrolled adsorption on the skin.

The coating of wool fabrics with permethrin containing nanogels is performed with different permethrin concentrations (Table 2) in a stable $\beta$-CD nanogel concentration. The permethrin content of the wool fabrics is determined quantitatively by HPLC analysis after extraction of the textile with pure methanol solution. Wool fabrics (3.79 g $\approx$ 200 cm$^2$) are treated with $\beta$-CD nanogel dispersions (3 mg/mL $\cong$ 4 wt % on the textile) containing permethrin with 0.00 mg/mL (0 wt % on the textile), 0.06 mg/mL (0.08 wt % on the textile), 0.12 mg/mL (0.16 wt % on the textile), 0.29 mg/mL (0.39 wt % on


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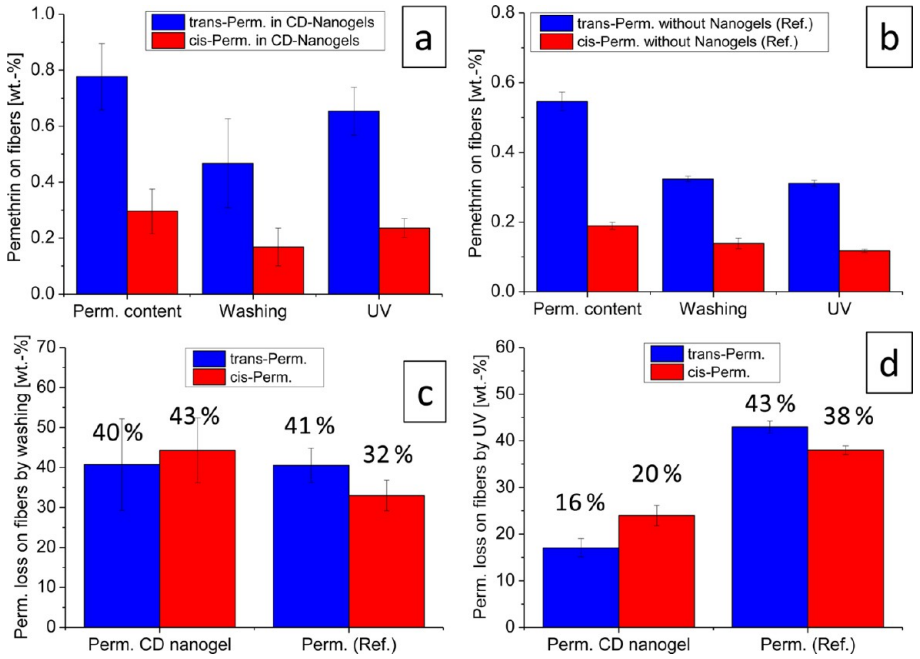


**Figure 7.** Permethrin (Perm.) content (in wt %, *trans*- and *cis*-permethrin) on wool fabrics after application, after a washing process and after 48 h of irradiation of fabrics treated with permethrin containing $\beta$-CD nanogels (a) and reference treated with permethrin containing insecticides (b) determined by HPLC analysis. The loss of permethrin from the fibers after washing (c) and after UV irradiation (d) in direct comparison to permethrin complexed in $\beta$-CD nanogels and noncomplexed permethrin.

the textile), 0.74 mg/mL (0.98 wt % on the textile) or 1.45 mg/mL permethrin (1.94 wt % on the textile). The determined permethrin concentrations in methanol extracts of treated wool fabrics are listed in Figure 6a.

In comparison to the linear order of the maximally expected values of the permethrin content in the aqueous dispersion, the concentration is similar to the calculated maximally possible concentration. Only the highest selected concentration of permethrin in the nanogels (1.94 wt %) results in lower permethrin content in the wool extracts than added. Thus, the higher calculated molar permethrin ratio in $\beta$-CD domains in the nanogels shows that the nanogel and especially the $\beta$-CD capacity for the complexation is reduced to take up a surplus of guest molecules. Both *trans*- and *cis*-permethrin are applied in the expected ratios on the fabrics due to the good adsorption properties of the $\beta$-CD nanogels on the fiber surface. Hence, the concentration of permethrin can be controlled on the keratin fibers by the application of CD nanogels from aqueous dispersion.

Figure 6b presents the results of the same samples measured after 3 years of storage at RT under ambient laboratory conditions. In the literature, it has already been reported that the stability of permethrin is low due to decomposition primarily by microorganisms but also by photolysis.[47] In water, permethrin is broken down by photolysis into 3-phenoxybenzyl alcohol (PBA) and dichlorovinyl acid (DCVA).[47] The average half-life range of permethrin in water is about 19−27 h. Permethrin can persist in sediments for approximately 1 year (1 $\mu$g/mL of 120 $\mu$g/mL after 1 year).[48] Indoor studies of permethrin applied in a thin layer to a surface showed that after 20 days of exposure to daylight, 60% of the permethrin remained on the surface.[49]

In our studies (Figure 6b), a loss of the *trans*- and *cis*-permethrin concentration is detectable after 3 years, but it is still active on the fabric. The trend of the permethrin content on the textile after 3 years is linear and comparable with the permethrin concentration applied from the CD nanogel dispersions. That means permethrin, especially *trans*-permethrin, is protected by complexation in CD nanogels against decomposition due to environmental influences. The permethrin decomposition can be delayed but not prevented. The sensitive organic compound is not permanently fixed to the textile and the release into the environment by evaporation, break down or restructuration decrease the permethrin concentration on the textile by and by. Interestingly, the loss of *cis*-permethrin concentration is in the same ratio as the one of the *trans*-permethrin concentration. This leads to the conclusion that the *trans*-permethrin:$\beta$-CD complex and the *cis*-permethrin:$\beta$-CD complex have the same stability in the nanogels.

**3.4. Permanence of Insecticides on Wool Applied after Complexation in Cyclodextrin-Containing Nanogels.** Wool fabrics, which were treated with permethrin loaded $\beta$-CD-containing nanogels, are investigated with regard to the fastness of the insecticides during washing (according to DIN EN ISO 105-C10) or to light (according to DIN EN ISO 105-B02) (Figure 7).

Washing tests show that after one washing process, about 40% of the *trans*- and *cis*-permethrin, which were incorporated in $\beta$-CD nanogels, are removed from the wool. These losses are similar to those determined for wool fabrics, which are treated with noncomplexed permethrin by conventional bath exhaustion procedure (98 °C, 1 h). Due to the water insolubility of permethrin, it can be concluded that the physically self-bonded permethrin loaded nanogels, which are redispersible in water, are removed from the fibers by washing. Thus, the treatment is not permanent; however, permethrin loaded nanogels can be reapplied easily onto textiles or other surfaces on demand.

Irradiation tests are made according to DIN EN ISO 105-B02. The results are also shown in Figure 7. Here, the

permethrin coated fabric is irradiated for 48 h, and the losses of permethrin during irradiation are determined by RP-HPLC analysis. In the case of wool fabrics that were treated with noncomplexed permethrin by conventional bath exhaustion procedure about 40% of *cis*- and *trans*-permethrin, losses are found after 48 h of irradiation. However, in the case of permethrin that was complexed by $\beta$-CD nanogels, markedly less permethrin is degraded during light exposure. Here, losses of about 16% of *trans*-permethrin and approximately 20% of *cis*-permethrin are determined for wool fabrics, which were treated with permethrin loaded $\beta$-CD nanogels after 48 h of irradiation. Hence, $\beta$-CD domains in the nanogel form inclusion complexes and act as protector for influences of the environment. These results show that permethrin, in particular *trans*-permethrin, is protected from light degradation by complexation in $\beta$-CD nanogels. The irreversible degradation of UV-sensitive permethrin by light exposure can be decreased for about 47% (cis) and 63% (trans) in comparison to the noncomplexed active ingredients.

It is known that the photodegradation of permethrin proceeds via two major reactions, i.e., isomerization of the cyclopropane ring and ester cleavage on photolysis.[47] The medium and the environment, e.g., the solvent, of the permethrin influence the photodegradation. The complexation of sensitive ingredients by cyclodextrin leads to changes of physical and chemical properties due to supramolecular bonding of guests by the host molecules. Furthermore, the complexation protects the guest molecule against environmental influences, e.g., molecular degradation due to light irradiation, which is explained by sterical fixation and shielding against the environment.[50,51] The complexation of *cis*- and *trans*-permethrin by the cyclodextrin groups in the nanogels leads to such sterical stabilization and shielding of the molecule, especially of the ester group by the CD cone so that the photodegradation due to photoisomerization is suppressed.

Wool fabrics treated with permethrin containing $\beta$-CD nanogels are also tested for color fastness upon light exposure. The yellowness index (G-DIN 6167) documents that a more or less pronounced lightening of the wool fabric was obtained upon exposure to light (here: negative values for the yellowness ΔG-DIN 6167 are measured).

In Figure 8, the color change of permethrin loaded fabric samples are presented. In the diagram, the change in yellowness of the untreated and the nanogel treated wool fabric are shown. The yellowness index of the fabric treated with the pure nanogel does not decrease as strongly as the untreated wool fabric when exposed to light. The fabric, which is treated with permethrin loaded CD nanogels, shows in comparison to the untreated fabric also a minimal decrease in the yellowness index after irradiation. It shows that photobleaching of the fabric is reduced in case of nanogel containing fabrics compared to the untreated wool sample. Obviously, the treatment with $\beta$-CD-containing nanogels or with permethrin loaded $\beta$-CD nanogels protects the wool fabrics from color changes when exposed to light.

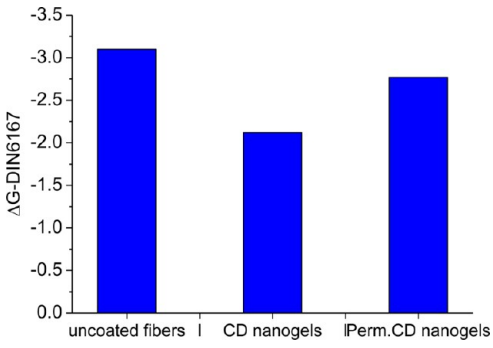


**Figure 8.** Color change (as change in yellowness ΔG-DIN 6167) of wool fabrics treated with permethrin loaded and unloaded $\beta$-CD-containing nanogels in comparison to the untreated wool fabric when exposed to light (DIN EN ISO 105-B02 (48 h)).

Merino wool exhibits a slightly yellowish color. The characteristic color is due to the presence of yellow chromophores, which are prone to bleaching upon light exposure under special conditions, e.g., short-time exposure, exposure behind window glass. It is known that photobleaching of wool depends on its yellowness, the more yellowish wool bleaches stronger than whiter wool.[52] Photobleaching of wool is caused by the action of radicals and oxygen active species which are formed during exposure to light.[52,53] We assume that the $\beta$-CD-containing nanogels protect the wool from photobleaching, due to scavenging of radicals or oxygen active species. This phenomenon is less pronounced in the case of CD-gels that contain complexed light-sensitive permethrin.

**3.5. Biological Effectiveness of the Insecticide Treatment.** Wool fabrics that were treated with $\beta$-CD nanogels complexed and with noncomplexed permethrin are investigated with regard to their biological effectiveness against the larvae of *Tineola bisselliella* (clothes moth) and of *Anthrenocerus australis* (Australian carpet beetle). The tests are performed by AgResearch Ltd., Hamilton, New Zealand, according to the Test Method Wools of New Zealand Method 25, which complies with the quality standard of ISO 3998-1977 (E). The effectiveness of the treatment is evaluated by the average mortality of the larvae in %, the mean mass losses of the fabric in % (compared to a control) and by visual assessment of the fabrics with regard to damages due to foraging.

Table 3 depicts the results of the biological tests against *Tineola bisselliella* (clothes moth) obtained for wool fabrics that are treated with $\beta$-CD nanogels and permethrin containing

**Table 3. Results of the Biological Tests of Wool Fabrics Treated with Permethrin Based Insecticides and with Permethrin Loaded $\beta$-CD Nanogels against Larvae of *Tineola bisselliella* According to Test Method Wools of New Zealand Method 25**

| wool fabrics | content of permethrin (wt %) | average mortality (%) | mean mass loss (% of the control) | visual assessment of fiber damages due to foraging |
|---|---|---|---|---|
| control | | 0.0 | 100 | strong damages |
| blank treatment[a] | | 0.0 | 86.7 | strong damages |
| $\beta$-CD-nanogels | | 1.7 | 172.3 | strong damages |
| perm.-$\beta$-CD nanogels | 0.94 | 100.0 | −0.3 | no visible damage |
| perm.-based insecticide[a] | 0.55 | 100.0 | −0.4 | no visible damage |
| perm.-based insecticide[a] | 0.34 | 100.0 | −1.6 | no visible damage |

[a]Blank treatment and treatment with permethrin by bath exhaustion procedure (98 °C, 1 h, pH 6).


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Table 4. Results of the biological tests of wool fabrics Treated with Uncomplexed Permethrin and with Permethrin Loaded β-CD Nanogels against Larvae of *Anthrenocerus australis* According to Test Method Wools of New Zealand Method 25

| wool fabrics | content of permethrin (wt %) | average mortality (%) | mean mass loss (% of the control) | visual assessment of fiber damages due to foraging |
|---|---|---|---|---|
| control | | 0.0 | 100 | moderate damage |
| blank treatment[a] | | 7.1 | 126.4 | moderate damage |
| β-CD nanogels | | 4.5 | 85.1 | moderate damage |
| perm.-β-CD nanogels | 0.94 | 40.0 | 7.5 | no visible damage |
| perm.-based insecticide[a] | 0.34 | 7.1 | 28.5 | no visible damage |

[a]Blank treatment and treatment with permethrin by bath exhaustion procedure (98 °C, 1 h, pH 6).

nanogels. For blank-treated fabrics and for wools that are treated with unloaded β-CD nanogels, no killing of the larvae is achieved. In the fabric sample, which is treated with the nanogels, shows even an increase of the mass loss of 72%. In these fabrics, large holes due to feeding damages are observed. However, for wool fabrics, which are treated with permethrin-loaded β-CD nanogels, 100% mortality of the moth larvae is determined, while no mass loss and no visible damage is found for the wool fabric after the test. From Table 3, it is apparent that the permethrin containing wool fabric is also effective with a concentration of 0.4% (wt %) with respect to the mortality of moth larvae. The complexed permethrin is applied here in a high concentration of 0.94 wt.-% onto the wool fabric, thus the sample passed the biological test without any reduction of the effectiveness.

The results of the biological tests against larvae of *Anthrenocerus australis* (Australian carpet beetle) are given in Table 4. Besides a control, a blank-treated and a wool fabric that is treated with an unloaded β-CD-containing nanogel, fabrics that are treated with permethrin or with permethin loaded β-CD nanogels are tested. The blank-treated and the wool fabric, which is treated with unloaded β-CD nanogels, show no effectiveness to prevent degradation by the larvae of the Australian carpet beetle. Wool fabrics that are treated with permethrin by bath exhaustion procedure and those that are treated with permethrin loaded β-CD nanogels are effective in killing the larvae of the beetles. As the concentration of permethrin on the wool fabric that is coated with β-CD nanogels with 0.94 wt % permethrin is much higher than that on the wool that is treated by the conventional bath exhaustion procedure (here: 0.34 wt % permethrin), a markedly better effectiveness against the larvae of the beetles is found in the first case. This is visible in the mortality of the larvae of 40% and a mass loss of the wool fabric of 7.5% relative to the control. Visual assessment of these wool fabrics treated with permethrin demonstrates that no holes or foraging damage is detected on the wool, so that it can be assumed that in future lower permethrin concentrations can be applied.

The biological tests show that permethrin containing β-CD nanogels as well as other substances containing permethrin provide good protection against moth larvae and carpet beetle larvae. Even in the presence of low concentrations of permethrin, high efficiency is obtained. In these studies, high concentrations of permethrin are tested in nanogels on wool fabrics. In future work, permethrin concentrations of 0.2−0.5 wt % offer the same effectiveness in order to optimize cost and performance.

## 4. CONCLUSIONS

In this work, we have demonstrated that nanogels can be used for coating and protection of keratin based fibers. We have chosen urethane cross-linked β-CD NCO-terminated sP(EO-*stat*-PO) nanogels that were developed and characterized regarding their ability to complex low molecular weight hydrophobic guest molecules before, for the uptake of permethrin, a commonly used insecticide. The inclusion complexation of permethrin by the CD units in the nanogels is proven by shifts in the UV and further by shifts in the NMR and the Raman spectra. Furthermore, the spectral data of the inclusion complexes lead to the conclusion that permethrin is shielded by the CD units in the nanogel structure. Release tests show that the guest molecule can be extracted by the use of a methanolic solvent, which enables the quantitative analysis by HPLC. Permethrin containing β-CD nanogels were applied onto wool or human hairs with homogeneous distribution and particle sizes of 100−200 nm. Through the use of higher concentrated nanogel dispersions for the coating process, a gel film was observed on the fibers. Keratin fibers can be treated with controlled permethrin concentrations from aqueous nanogel dispersion. Washing tests showed that the insecticide was released during washing and removed from the fibers. However, irradiation experiments revealed that the complexation of permethrin by β-CD nanogels results in light protection of the light-sensitive ingredient. The irreversible photodegradation of permethrin can be decreased for about 47% (*cis*-permethrin) and 63% (*trans*-permethrin) in comparison to the noncomplexed active ingredient. Furthermore, application of β-CD nanogels onto wool fabrics reduces photobleaching when exposed to light. The biological tests demonstrated that permethrin loaded CD nanogels provide protection of wool from damage by the larvae of clothes moths or carpet beetles in the same way like noncomplexed permethrin. The biological effectiveness of the insecticide is not affected by the complexation by β-CDs. Our method is straightforward, robust, and generic with respect to the active compound and thus opens an attractive alternative for the treatment and protection of keratin based fibers as well as other materials.

## ■ ASSOCIATED CONTENT

### Supporting Information

Spectroscopic data and spectra of the synthesized β-CD-containing nanogels and of the corresponding β-CD nanogels after complexation of permethrin, a picture of the nanogel dispersion, and the electron microscopic image of uncoated human hairs. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Authors

*K. Schaefer. E-mail: schaefer@dwi.rwth-aachen.de.
*M. Moeller. E-mail: moeller@dwi.rwth-aachen.de.

### Notes

The authors declare no competing financial interest.

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