Article

Pullulan Derivatives as Softening and Cleaning Additives for Laundry Detergents

Marcellino D'Avino, Ruth Chilton, Gang Si, Mark R. Sivik, and David A. Fulton*

Read Online

ACCESS | Metrics & More | Article Recommendations

ABSTRACT: 2-in-1 laundry formulations have become popular among consumers as these represent a great alternative to standard detergents offering both cleaning and softening benefits in one product. Deposition aid polymers are crucial additives of a 2-in-1 formulation as they enhance the deposition of softness active ingredients. In this work, a novel class of pullulan derivatives grafted with cationic moieties (CatPs) have been synthesized and their softness and cleaning performance in a 2-in-1 laundry detergent have been assessed. Results show that the addition of cationic appendages is indispensable to observing an increase in textile softness. Compared with similar cationic polysaccharides, CatPs were also able to deliver better antiredeposition performance on both cotton-based and synthetic garments, probably on account of their higher capacity to stabilize particulate soil suspensions. The investigation of the solution behavior of CatPs with a typical laundry formulation revealed a phase separation (coacervation) occurring as a result of the association of the cationic pullulans with anionic surfactants. Results highlighted the dependence of this phenomenon on the polymer concentration and composition. This work demonstrates that CatPs represent a promising biorenewable additive for laundry detergent, providing both effective softness and cleaning performance.

INTRODUCTION

Fabric softness is one of the most frequently used terms in describing clothing comfort by consumers. Textiles used to produce consumer garments typically go through various physical and chemical finishing steps to improve their softness properties. Regularly treating the garments with appropriate high-quality fabric care products can maintain such properties and therefore increase the longevity of the garments.[1]

Added through the rinse, fabric softeners or fabric conditioners are very effective in providing fabrics with various desirable characteristics.[2] Among these, the ability of softeners to improve textile softness and freshness is undoubtedly the most important. Fabric softeners are also reported to prevent or reduce the buildup of electrostatic charges on textiles by improving fabric surface conductivity and therefore reducing static between fabrics. Furthermore, softeners are known to extend fabrics' durability by lowering the interyarn friction and reducing the damage caused during the tumble-drying stage. Finally, when working in combination with perfumes, fabric conditioners are able to provide garments with distinctive fragrances.[3]
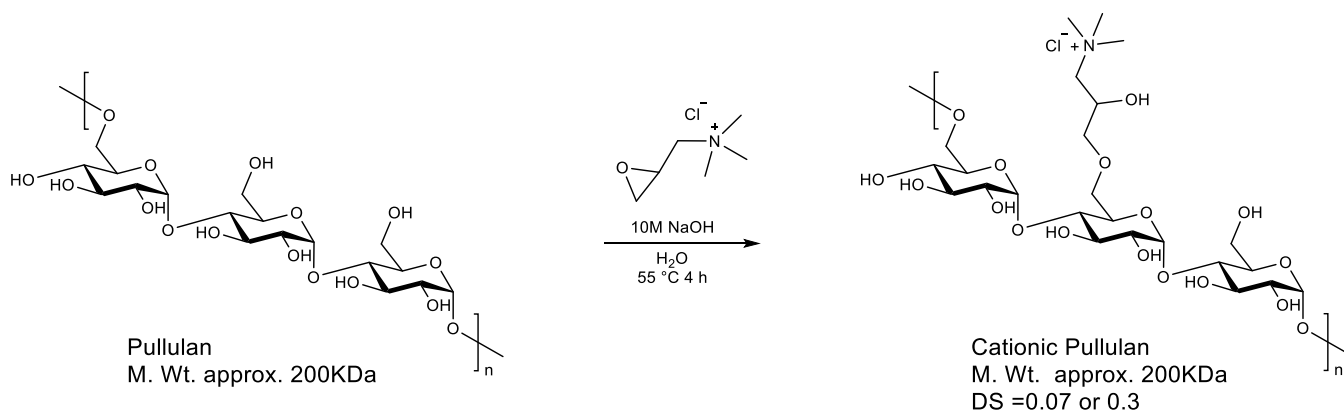
Although technically very effective, some consumers may prefer not to use a separate fabric softener product during the rinse cycle, in addition to the cleaning detergent utilized in the main wash. A 2-in-1 detergent product, namely, a detergent

capable of providing both cleaning and softening effects, may become the product choice for these consumers. Conventional softening agents, such as DADMACs and esterquats, are not typically used in 2-in-1 products on account of their strong interactions with anionic surfactants; hence, these are replaced with different softness active ingredients, such as fatty acid, anionic surfactant, or silicones. To increase the deposition of such active specimens on fabrics, a deposition aid polymer is generally used. Ideally, a deposition aid polymer should be able to selectively deposit the soft active ingredients on fabric and prevent the resettling of stain back onto the treated garments. On a molecular level, the deposition aid polymer actively participates in the formation of an insoluble complex or coacervate with the softening agent that deposits from the washing liquor onto the treated garments, thus providing the observed softening effect.

Scheme 1. Synthesis of Cationic Modified Pullulan (CatP)

Polulan
M. Wt. approx. 200KDa

10M NaOH
H$_2$O
55 °C 4 h

Cationic Pullulan
M. Wt. approx. 200KDa
DS =0.07 or 0.3

Polysaccharides are naturally derived and made from biogenic carbon, thereby being an interesting platform for the development of novel laundry additives. Cationic modified ethers of water-soluble cellulose derivatives (e.g., hydroxyethyl cellulose) have recently been found to deliver softness benefits on cotton-based fabrics when tested in combination with cationic surfactants.[4] Furthermore, it has been discovered that natural polymers such as cationic guar gum or hydroxypropyl guar gum (both extracted from natural plants) are able to increase the softness of various textiles by contemporarily reducing the amount of surfactants required to achieve similar results in the absence of polymers.[5]

Among natural polymers, pullulan has recently gained great interest. Pullulan (Scheme 1) is a water-soluble polysaccharide produced by the fungus *Aureobasidium pullulans*. It is characterized by linear chains of maltotriose subunits (i.e., three glucose units connected by α-1,4 glycosidic bonds). Each trimetric subunit is in turn connected to another subunit by α-1,6 glycosidic bonds.[6] In contrast to other polysaccharides, pullulan exhibits excellent water solubility and, hence, does not require substantial chemical modifications to improve its water solubility. As a consequence, pullulan represents a great candidate for the design of biobased laundry additives. In this work, we have synthesized cationic pullulan derivatives displaying different levels of cationic appendages and assessed both their behavior as a fabric softener additive and washing performance. Results demonstrate that the introduction of cationic moieties onto the pullulan backbone significantly increases its ability to deliver softening benefits on cotton-based textiles even at a low grafting level. Surprisingly, cationic modified pullulan displayed better antiredeposition performance than similar cationically modified polysaccharides (i.e., Ucare LR-400, cationic hydroxyethyl cellulose), especially on polyester garments. Turbidity measurements were used to shed light on the antiredeposition results. These revealed a better capacity of cationic modified pullulan derivatives to stabilize particulate soil suspensions than that of Ucare LR-400. Furthermore, the solution behavior of cationic pullulan was investigated by exploring its interaction with both a laundry detergent formulation and a single anionic surfactant (sodium dodecyl sulfate) via UV−visible absorbance. Results suggested that under opportune conditions, cationic pullulan and anionic surfactants form a coacervate that resulted in an observable phase separation. The effects of concentration and the polymer architecture on the coacervate formation were also investigated.

■ EXPERIMENTAL SECTION

Materials and Methods. Pullulan and sodium dodecyl sulfate (SDS, >85%) were purchased from Tokyo Chemical Industry UK Ltd. According to the supplier information, pullulan is characterized by an average molecular weight of approximately 200,000 Da. Sodium hydroxide, acetone (>99%), concentrated hydrochloric acid, glycidyl trimethylammonium chloride (GTAC, >90%) and dialysis membrane tubing (6000−8000 Da MWCO) were purchased from Sigma-Aldrich. Cationic hydroxyethyl cellulose, commercially available as Ucare LR-400 (400,000 Da),[7] and a typical laundry formulation without polymeric additives, was provided by P&G (Newcastle Innovation Centre). The latter is a complex mixture of nonionic and anionic surfactants whose composition has been disclosed in the patent literature.[8] Polyester sheets loaded with BS2004 soil (SBL) were acquired from WFK Testgewebe GmbH. BS2004 soil was prepared following the composition provided by the supplier (WFK Testgewebe GmbH). All chemicals were used without further purification.

Synthesis of Cationic Pullulan (CatPA and CatPB). A 100 mL round-bottom flask equipped with a magnetic stirrer and a condenser tube was charged with pullulan (7.0 g, 43.20 mmol) and 35 mL of water. The mixture was stirred at room temperature for 30 min to allow pullulan to fully dissolve. The solution was cooled to 4 °C in an ice bath. Then, 25 mL of a aqueous sodium hydroxide solution (10 M) was added dropwise via a syringe and the mixture was stirred for 20 min. Glycidyl trimethylammonium chloride (GTMAC, 3.234 g, 0.021 mmol) was added dropwise via a syringe, and the reaction was heated to 55 °C for 4 h. After being cooled to room temperature, the reaction mixture was neutralized with concentrated hydrochloric acid and precipitated in acetone. The crude product was collected by vacuum filtration, washed with acetone, and then dried at 70 °C for 24 h under reduced pressure. Crude cationic pullulan (**CatPA**) was dissolved in 60 mL of water, and the obtained solution was dialyzed against water for 4 days, and then freeze-dried to afford a pale-yellow solid (4.94 g, 48%). Sample **CatPB** was obtained by an identical procedure while changing the amount of GTMAC used (4.80 g, 16%).

Characterization. ^{1}H NMR and ^{13}C NMR spectra were recorded on an Avance Bruker 400 MHz spectrometer operating at 25 °C. Samples were prepared by dissolving 5 mg of the product in 600 μL of D$_2$O. Dissolution occurred immediately and clear solutions were obtained.

FTIR spectra (in the range of 400−4000 cm^{-1} wavenumbers) were recorded using an IRAffinity-1S Fourier transform infrared spectrophotometer equipped with an ATR (attenuated total reflectance) sampler at 4 cm^{-1} spectral resolution. For each experiment, 50 scans were collected and averaged. Samples were dried overnight in a vacuum oven at 70 °C before each measurement.

Elemental composition was evaluated using a Thermo Fisher Scientific CHN elemental analyzer. From the measured N%, the degree of substitution (DS) was calculated according to eq 1, where M_{RU}: molar weight of the repeating unit of pullulan, M_{GTAC}: molar weight of the cationic substituent.[8]

$$ DS = \frac{\frac{\%N}{100} \cdot M_{RU}}{14 - \frac{\%N}{100} \cdot (M_{GTAC} - 1)} \tag{1} $$

Antiredeposition Performance Test. Antiredeposition tests were performed as described in previous work.[8,9] Briefly, polyester (PE), knit cotton (KC), polycotton (PC), and polyspandex (PS) clean tracers (5 × 5 cm^2 garments) were washed under controlled conditions in an automatic tergotometer equipped with 10 washing pots in the presence of a **CatPA** or **CatPB** solution and a typical laundry detergent formulation. Each washing load was made up of: four garments for each type of textile; a sufficient number of polyester squares stained with BS2004 soil (SBLs) and an adequate number of KC and PC swatches to reproduce consumers' washing conditions. Test conditions are summarized in Table 1. At

Table 1. Summary of Antiredeposition Test Conditions

polymer concentration	laundry detergent concentration	washing cycle parameters	water conditions
50 ppm	1950 ppm	40 min washing	21 gpg
		2 × 5 min rinse	35 °C
		300 rpm	

the end of each washing cycle, exhausted SBL garments were replaced with new ones. A new washing cycle was performed. The same process was repeated four times. Finally, tracers were collected and dried under humidity and temperature control (50% RH and 20 ± 2 °C).

The whiteness degree of fabrics was monitored via image analysis. A reflection spectrophotometer (Konica Minolta: CM-3630A) was used to collect tracer images before and after the washing cycle. The color of each fabric was expressed in terms of the coordinates L_n^*, a_n^*, and b_n^* defined in the CIELAB color system. The whiteness index (WI) was calculated by applying the following equation:

$$ WI = Y + 800(x_n - x) + 1700(y_n - y) \tag{2} $$

where Y is the luminance factor, while x and y are the color coordinates of the observed garment defined in the Y_{xy} color space. These parameters can be calculated by opportunely converting the measured values of L_n^*, a_n^*, and b_n^* which correspond to Y, x, and y, respectively. x_n and y_n are the color coordinates of the lighting source used (D65). Finally, whiteness results were displayed as the difference (ΔWI) between the WI of tracers washed with **CatPA** or **CatPB** in the presence of the detergent formulation and the WI of tracers washed with the detergent formulation only. High soil antiredeposition performances are observed with high ΔWI values.

Soil Suspension Stability. The ability of **CatPA** or **CatPB** to maintain soil in suspension was explored via a Turbiscan optical analyzer (Formulaction, L'Union, France). Stock solutions of **CatPA** or **CatPB** and a typical laundry detergent formulation were prepared in Milli-Q water (5% w/w). 0.06 mL of each solution was transferred to a 30 mL glass vial containing 0.08 g of BS2004 soil. Hard water (21 gpg) was added to bring the total volume of the solution to 20 mL. The final concentrations of **CatPA** or **CatPB** and soil were 150 and 4000 ppm, respectively, and the concentration of the laundry detergent was 2000 ppm. Then, the vial was sonicated in an ultrasonic bath for 20 min at 35 °C. Immediately after the sonication, the soil suspension was monitored by collecting T and Bs profiles every min for 1 h. The stability of each suspension was quantitatively evaluated in terms of the Turbiscan stability index (TSI), a parameter used to study the destabilization phenomenon occurring in a colloidal system.[10] The TSI is based on an integrated algorithm that takes into account the evolution of T or Bs signals over time and along the height of the vial. It is calculated according to the following equation:

$$ TSI(t) = \frac{1}{N_h} \sum_{t_i=1}^{t_{max}} \sum_{z_i=z_{min}}^{z_{max}} |Bs(t_i, z_i) - Bs(t_{i-1}, z_i)| \tag{3} $$

where z_{max} and z_{min} are the higher and the lower limits of the area of the vial's height where the TSI is calculated; N_h is the number of points along the vial height; t_{max} is the time at which the TSI is quantified. High TSI values are generally observed for highly unstable systems undergoing destabilization processes, such as creaming, coalescence, or sedimentation. On the other hand, low TSI values emerge from highly stable systems.

Coacervation Formation of CatP with a Laundry Detergent and SDS. The behavior of solutions containing **CatPA** or **CatPB**, a typical laundry detergent, or SDS was monitored using a Brinkmann PC-950 colorimeter equipped with a 76.2 cm optic fiber and a 2 cm stainless steel probe. Stock solutions of **CatPA** or **CatPB** were prepared in Milli-Q water (5% w/w). The latter were further diluted in 350 mL of demineralized water into a 500 mL beaker to various concentrations. A stock solution of a typical laundry formulation and of SDS were prepared in Milli-Q water (50,000 ppm). 0.1 mL of this stock solution was transferred into the 500 mL beaker containing the **CatPA** or **CatPB** solution. The mixture was stirred and allowed to stabilize until the corresponding optical transmission value, recorded by the colorimetric probe, remained constant. Further stepwise additions of the laundry detergent stock solution (or SDS solution) were performed. Finally, the collected transmission values were reported as a function of either the laundry detergent level or the SDS content (ppm).

Fabrics Softness Assessment: Secant Modulus. The ability of **CatPA** or **CatPB** to deliver fabric softness benefits was evaluated by monitoring the secant modulus of polycotton fabric swatches treated with **CatPs** solutions in the presence of a typical laundry detergent formulation. 32 × 32 cm^2 cotton cloths (CT) were acquired from Calderon Textiles (Indianapolis, Indiana, USA). Twenty-eight × 28 cm^2 knitted polycotton (PC) was purchased from Centre for Test materials (the Netherlands). Fabrics were washed in a Miele 1714 washing machine under a cotton 40 °C short cycle at controlled water hardness. All test conditions are listed in

Table 2. Washing loads were composed of: five CT swatches, four PC garments and 2.5 kg mix of cotton/polycotton textiles

Table 2. Summary of Polycotton Pretreatment Test Conditions

polymer concentration	laundry detergent concentration	wash cycle parameters	water conditions
20 ppm	2000 ppm	50 min washing 3 × 5 min rinse 300 rpm	21 gpg 40 °C

to simulate consumers' washing conditions. After each washing cycle, the full load was tumble dried for 30 min. The same process was repeated six times.

Dried polycotton fabrics were cut into 2.5 cm wide and 10 cm long strips. All fabrics were equilibrated under the temperature and humidity condition of the test location for at least 6 h prior to the data collection (21 °C 50% RH). The secant modulus of fabrics was measured using an Instron 3342 tensile and compression tester (Instron Corp., Norwood, Massachusetts, USA) equipped with a 100 N load cell. After each garment was loaded into the pneumatic grip of the tester, an initial tension of about 0.05 N was applied to remove any observable slack. Each strip was tested with a two-step protocol. An initial 35% strain was achieved at a constant rate of 150 mm/min, followed by a 0% strain restored at a constant rate of 150 mm/min. This sequence of two successive deformations describes a hysteresis loop. Each specimen underwent four hysteresis cycles. The fourth hysteresis cycle was used to evaluate the secant modulus, with the latter defined as the slope of the line that intersects the stress−strain curve between 0% and 35% strain. Nine replicates (fabric specimens) were analyzed for each tested polymer. The resulting secant modulus values were averaged to yield an average secant modulus.[11]

■ RESULTS AND DISCUSSION

Synthesis and Characterization. The synthesis of cationic pullulan was performed (Scheme 1) under homogeneous conditions.[12,13] Glycidyl trimethylammonium chloride (GTMAC) was used as a cationizating agent. Pullulan (molecular weight of ~200 kDa) was initially dissolved in water and then alkalinized with aqueous NaOH in order to activate its hydroxyl groups. Two cationic pullulans (**CatPA** and **CatPB**, possessing different degree of substitution (DS)) were prepared by adjusting the amount of cationizating agent used. It would be desirable to also produce cationic pullulans of different molecular weights, but unfortunately at the time of our study 200 kDa pullulan is the only MW commercially available to us. Details of the products obtained are summarized in Table 3.

The cationic pullulans **CatPA** and **CatPB** were characterized via FTIR, ^{1}H NMR, and ^{13}C NMR spectroscopies (see the SI for ^{13}C NMR spectra). The FTIR spectra of pure pullulan and **CatPA** and **CatPB** are displayed in Figure 1. All samples showed signals characteristic of natural polymers.[14] The broad peak centered at ~3300 cm^{-1} corresponds to the stretching vibration of −OH; the band observed at ~2900 cm^{-1} was assigned to saturated C−H vibrations; the stretching vibration of C−O−C was registered at ~1020 cm^{-1}. The successful grafting of cationic appendages was confirmed by the presence of a new signal at 1477 cm^{-1} corresponding to the bending of

Table 3. Summary of Cationic Pullulans (CatP) Prepared by the Homogeneous Etherification of Pullulan Using Glycidyl Trimethylammonium Chloride

product code	cationic pullulan (CatP)					
	DS^a	DS^b	yield (%)	pull:GTAC^c (mol: mol)	product obtained (g)	N^d (%)
CatPA	0.07	0.16	48	2	4.94	0.59
CatPB	0.30	1.15	16	23	4.80	1.99

^{a}Degree of substitution of cationic moieties (DS), based on elemental analysis. ^{b}Degree of substitution of cationic moieties (DS), based on ^{1}H NMR. ^{c}Molar ratios between pullulan and the modifying agents. ^{d}Nitrogen percentage (N%) as measured by elemental analysis.
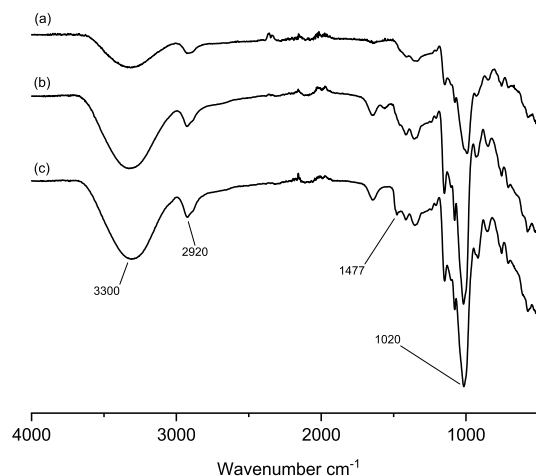
Figure 1. FTIR spectra of (a) pullulan and (b, c) cationic modified pullulan (**CatPA**, **CatPB**).

the C−H bonds of the three methyl groups. **CatPA** and **CatPB** displayed almost superimposable FTIR spectra (Figure 1b versus c). A more intense 1477 cm^{-1} band was observed for **CatPB** because of its higher degree of substitution. The successful grafting of cationic moieties onto the pullulan backbone was also confirmed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of pure pullulan is shown in Figure 2 a. The signals at 5.41, 5.35, and 4.96 ppm are associated with the three anomeric protons of each maltotriose unit. The collection of signals ranging from 4.04 to 3.45 ppm arises from the protons of each glucose ring. The introduction of cationic appendages resulted in the appearance of new signals. The signal at 4.42 ppm (Figure 2b,c) was attributed to the methine proton of the glycidyl trimethylammonium chain, while the intense signal at 3.26 ppm arises from the protons of the three methyl groups of the appended moieties. Increasing the feed ratio between pullulan and GTMAC resulted in higher degrees of substitution, as confirmed by the increasing percentage of N recorded via elemental analysis and by the enhancement of the intensity of signals corresponding to grafted appendages (Figure 2b versus c). Analysis of the ^{13}C NMR spectra suggests that the grafting of the GTMAC moieties predominately occurred at position 6 of the glucose ring. Indeed, the C-6 signal was observed to shift from 60 to ~67.5 ppm, implying the presence of cationic groups.[13] As reported in Table 3, the DS values calculated via ^{1}H NMR are significantly higher than those obtained through elemental analysis. This is a consequence of the intense line broadening observed for samples **CatPA** and **CatPB**.
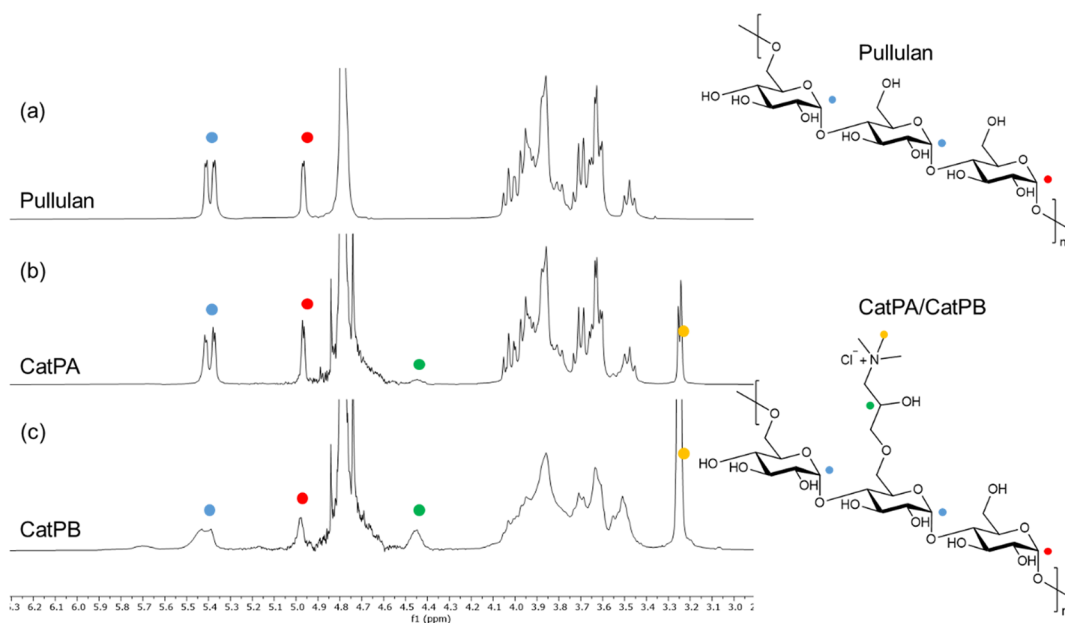
Figure 2. ^{1}H NMR spectra (400 MHz, D$_2$O) of (a) pullulan and (b, c) cationic modified pullulan (**CatPA**, **CatPB**).

Fabrics Softness Assessment: Secant Modulus. With useful quantities of cationic modified pullulan derivatives available, their ability to modify fabric has been assessed. Fabric hand can be defined as the estimated quality of a garment assessed from the sense of touch.[15] It is the result of multiple complex factors (e.g., type of fibers, fiber behavior, friction etc.), and therefore, it is difficult to evaluate quantitatively. Although fabric hand has been traditionally estimated[16] by sensory assessments (individuals would use properties such as softness, stiffness or harshness to subjectively assess fabrics characteristics), objective numerical descriptors are indispensable to steer manufacturers toward the design and production of textiles with consistent quality. Over the years, researchers have tried to correlate fabrics' attributes with measurable mechanical properties. The most relevant method in this field is the Kawabata method, known as Kawabata Evaluation System (KES), that proposes a relationship between fabric mechanical properties (measured with a KES-FB instrument) and fabric hand characteristics.[16] Specifically, the KES comprises sensitive equipment to evaluate mechanical and surface properties of a wide spectrum of fibrous materials, e.g., woven fabrics, knitted fabrics etc. Among fabric attributes, softness is one of the most important tactile properties. Results from consumer tests have demonstrated that fabric softness correlates with textile elasticity, with the latter evaluated in terms of secant modulus. It has been found that low secant modulus values are associated with higher softness results.[16] To assess the ability of **CatPs** derivatives to provide softness benefits, the secant modulus of polycotton (PC) fabrics conditioned with **CatPs** solutions was measured with an Instron 3342 tensile tester.

Figure 3 shows a comparison of the secant modulus of polycotton (PC) fabrics treated with unmodified pullulan (orange), **CatPA** (green), **CatPB** (white), and a typical laundry formulation only (red). PC garments conditioned with unmodified pullulan displayed a reduction of the secant modulus with respect to fabrics treated solely with the laundry formulation. Introduction of cationic moieties onto the pullulan backbone caused a further reduction of the secant
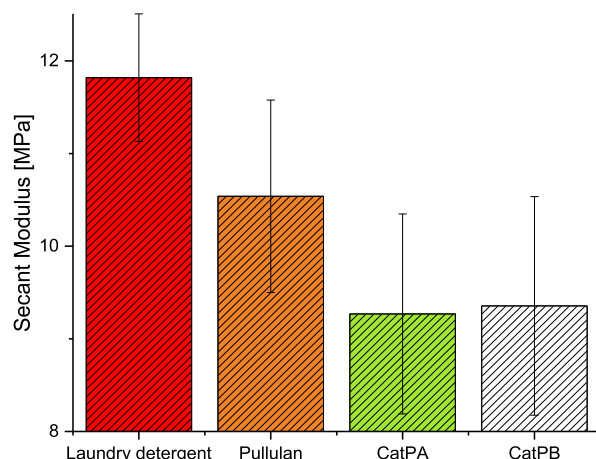

Figure 3. Secant modulus of polycotton (PC) fabrics conditioned with pullulan (orange), **CatPA** (green), **CatPB** (white), and laundry detergent (red). Error bars are calculated as a product of the standard error $\left(\frac{\sigma}{\sqrt{n}}\right)$ and the t value associated with each specimen value distribution. CatPs concentration: 20 ppm; laundry detergent concentration: 2000 ppm.

modulus, as observed for **CatPA** (green) and **CatPB** (white). The secant modulus quantifies the tensile stiffness of a textile.[17] Low secant modulus values are associated with an increase in fabric extensibility. The variation of the tensile characteristics of PC fabrics treated with **CatPA** and **CatPB** is most likely on account of the adsorption of the cationic modified polymers onto the surface of fibers. This adsorption provides a lubrication effect that reduces the friction between fibers, thus causing the observed increase in extensibility.[15,18] Increasing the number of cationic groups (Figure 3, **CatPA** vs **CatPB**) does not provide any noticeable improvement in fabric softness.

Antiredeposition Performance Test. In order to assess the effect of the presence of CatPs on the antiredeposition ability of a model laundry formulation, an antiredeposition test was performed. In a typical antiredeposition test, clean fabric

swatches are washed together with stained fabrics in the presence of a laundry formulation containing antiredeposition additives. During the washing cycle, clean swatches adsorb materials released by stained fabrics. At the end of the washing cycle, the color change of clean fabric swatches is quantified (ΔWI variation) to assess the antiredeposition performance of the additive. In this study, antiredeposition tests were performed on both synthetic and cotton-based textiles, namely, polyester (PE), knit cotton (KC), polycotton (PC), and polyspandex (PS) fabrics. The antiredeposition ability of **CatPB**, chosen as a representative of cationic modified pullulan, was compared with that of a commercially available cationic hydroxyethyl cellulose (Ucare **LR-400**). Whiteness indexes (WIs) were calculated via image analysis. Results are displayed in Figure 4A.
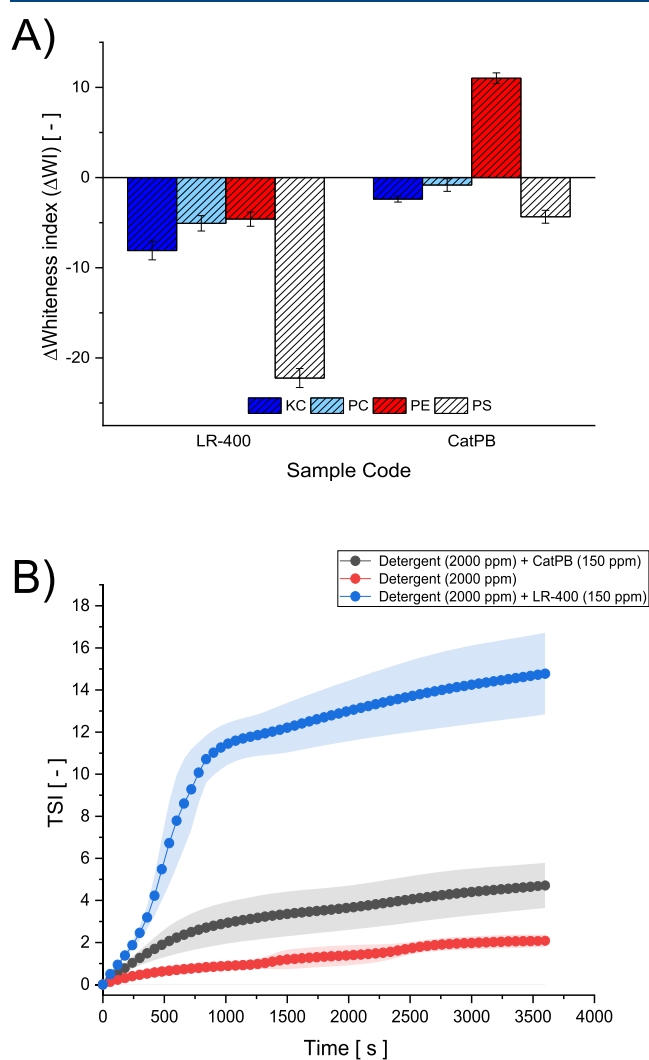
Figure 4. Antiredeposition test results. Whiteness index variation (ΔWI) of knit cotton (blue, CK), polycotton (light blue, PC), polyester (red, PE), and polyspandex (white, PS) tracers washed with a laundry detergent formulation in the presence of **CatPB** and LR400 (A). CatPs concentration: 50 ppm; laundry detergent concentration: 1950 ppm. Turbiscan stability index (TSI) as a function of time (s). Evolution of the TSI index of samples **CatPB** and **LR400** (150 ppm) compared with the TSI index of a laundry detergent (2000 ppm) in the absence of polymers (B).

As shown in Figure 4A, LR-400 does not provide any noticeable antiredeposition benefits for all types of fabrics. Indeed, a negative variation of the WI was observed for all of the garments treated with **LR-400**. Negative ΔWI values arise from textiles displaying a darker color after the washing cycle as a result of the adsorption of soil onto the fabric surface. This is probably a consequence of the weak capacity of **LR-400** to maintain soil in a suspension in the washing liquor. Conversely, textiles conditioned with **CatPB** displayed, on average, higher WI indexes for all types of fabrics. Interestingly, a positive WI variation was observed for PE swatches treated with **CatPB**. We speculate that this result is a consequence of the better adsorption of cationic modified pullulan onto polyester fabrics.

Soil Suspension Stability: Results. The capacity of polymeric aids within a laundry formulation to stabilize soil suspensions is a crucial factor in determining the cleaning effectiveness of a washing cycle. In an attempt to interpret the antiredeposition results, the ability of **CatPB** and **LR-400** to maintain BS2004 soil in suspension was explored. In this work, the stability of BS2004 soil suspensions was monitored by following the behavior of the Turbiscan stability index (TSI) for 1 h.[14] The results are summarized in Figure 4B where the TSI values of a laundry detergent in the presence of **CatPB** (black) and **LR-400** (blue) are displayed and compared with the TSI of a laundry detergent only (red). The laundry detergent formulation, containing predominately anionic and nonionic surfactants, exhibited the lowest TSI values among all the monitored samples. Low TSI values are associated with systems characterized by good colloidal stability. A slight increase in the TSI values was observed for **CatPB** suggesting that the introduction of a cationic modified polymer affects the stability of the soil suspension. Nonetheless, no noticeable phase separation was observed. Conversely, complete segregation of the suspended soil from the aqueous solution was detected for the laundry detergent with **LR-400**. Indeed, the corresponding TSI values initially (time <200 s) increased at a rate comparable with that observed for the other samples but then steeply rose to about 12 units within 15 min. A further steady increase at a lower rate was recorded throughout the rest of the experiment. These observations suggest that the interaction of the cationic polymers with surfactants governs their capacity to stabilize BS2004 soil suspensions. Despite having similar charge levels (**LR-400** DS = 0.25 and **CatPB** DS = 0.30), **LR-400** possesses a much higher molecular weight (~400 kDa) than **CatPB** (~200 kDa). Variation of the molecular weight can significantly affect the phase behavior of an aqueous mixture of cationic polyelectrolyte with anionic surfactants. Indeed, increasing the polymer chain length lowers the anionic surfactant concentration required to observe a macroscopic phase separation (coacervation).[19] We speculate that in the case of **LR-400**, the tested laundry detergent concentration was sufficient to trigger complete association with anionic surfactants, causing the formation of a coacervate. Consequently, in the absence of actively stabilizing agents, soil material easily aggregates and precipitates in the washing liquor. Furthermore, on account of its higher molecular weight, sample **LR-400** behaves as a flocculant. It binds with negatively charged particles of BS2004 soil (i.e., clay and carbon black) promoting their association into larger aggregates (a phenomenon called bridging).[20,21] These two complementary factors contributed to the sedimentation of BS2004 soil particulate during a washing cycle, causing its deposition on fabrics. As a result, fabrics treated with **LR-400** exhibited a
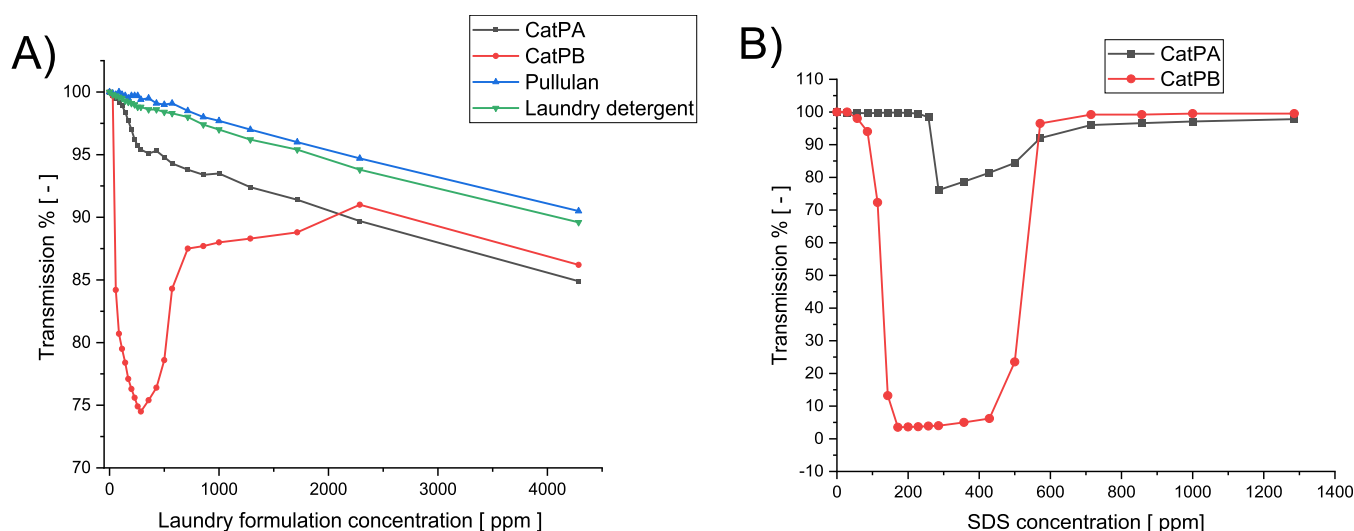
Figure 5. Transmission values for modified cationic pullulan solutions as a function of a laundry detergent concentration (A); transmission values for modified cationic pullulan solutions as a function of sodium dodecyl sulfate (SDS) concentration (B).

darker color and therefore higher ΔWI variations than fabrics conditioned with **CatPB**.

Coacervation Formation: Results. It is known that the association of anionic surfactants with cationic polymers can lead to a coacervation and subsequent macroscopic phase separation.[22] The extent of this phenomenon is strongly dependent on polyelectrolyte architecture (i.e., surface charge, molecular weight) and concentration.[19] The utilization of mixtures of oppositely charged species (e.g., cationic polyelectrolytes and anionic surfactants) has been extensively described over the years in various commercial applications such as papermaking, fabric care, personal care, etc. In the case of 2-in-1 laundry detergent, the coacervation of the deposition aid polymer with the anionic surfactants is crucial to enhancing the deposition of the surface active ingredients. Here, the behavior of aqueous solutions of **CatPA** and **CatPB** in the presence of a laundry detergent formulation or single anionic surfactant (i.e., sodium dodecyl sulfate or SDS) was monitored using a Brinkman PC-950 probe colorimeter. Results are reported in Figure 5A,B.

The variation in the transmitted light of an aqueous solution of **CatPA** and **CatPB** upon addition of a laundry detergent are displayed in Figure 5A and compared with that of an aqueous solution of unmodified pullulan. No significant differences were observed between pullulan and the laundry detergent. Indeed, in both cases, the intensity of the transmitted light progressively decreased as the amount of surfactant increased. The introduction of cationic moieties onto the pullulan backbone drives the coacervation of the modified poly-saccharides with the anionic surfactants that populate the laundry formulation, as observed in Figure 5A (black and blue lines). For both **CatPA** and **CatPB**, the intensity of the transmitted light initially decreased as the surfactants started to bind onto the polymer. The association between the hydrocarbon chains of bound surfactants, driven by hydro-phobic interactions, acts as cross-linking agents and triggers the organization of the polymer chains into a three-dimensional network.[19,23] Gradual addition of the laundry formulation caused a further decrease in transmission due to the formation of larger aggregates between the cationic polymers and anionic surfactants until a minimum transmission value was reached

(charge neutralization).[19,23] Finally, adding an excess of the laundry formulation induced the redissolution of the aggregates, resulting in an increase in the intensity of the transmitted light. On a molecular level, above the charge neutralization point, anionic surfactants assemble into micelles exposing their charged moieties outward. As a consequence, the excess of negative charge and the advantageous exposure of water molecules slowly induces the redissolution of the large polymer−surfactant complexes into smaller particles resulting in a reduced turbidity of the monitored solutions.[19,23] Nevertheless, crystal clear solutions could not be obtained on account of the cloudiness of the starting laundry formulation stock solutions.

The variation in the transmitted light of an aqueous solution of cationic pullulans (fixed at 100 ppm) upon addition of (SDS) is displayed in Figure 5B. Similarly to previous observations in relation to the laundry formulation, for both **CatPA** (Figure 5B, black line) and **CatPB** (Figure 5B, red line), the observed transmission initially decreased and then increased when titrated with a SDS solution. Further additions above the charge neutralization point completely restored the original transmission values, producing crystal clear solutions. Varying the number of cationic appendages from **CatPA** (DS = 0.07) to **CatPB** (DS = 0.30) significantly affected their solution behavior in the presence of SDS. Indeed, a decrease in the concentration corresponding to the onset of the phase separation and an increase in the concentration equivalent to the charge neutralization point was observed going from **CatPA** to **CatPB**.[24] As previously observed, the extent of the phase separation phenomenon occurring in a system comprising oppositely charged species is governed by both their chemical properties and concentrations. Pseudo phase diagrams can be built by monitoring the turbidity of their solution as a function of concentration. The pseudo phase diagrams of **CatPA−SDS** and **CatPB−SDS** along with pictures of the polymers-SDS mixtures are depicted in Figure 6A,B, respectively. The vertical axes report the polymer concen-tration, while the horizontal axes report the SDS concentration. As displayed in Figure 6A, three distinctive regions can be identified: region I where **SDS** and **CatPB** coexist as a single transparent phase; region II where **SDS** and **CatPB** associate

A)

B)
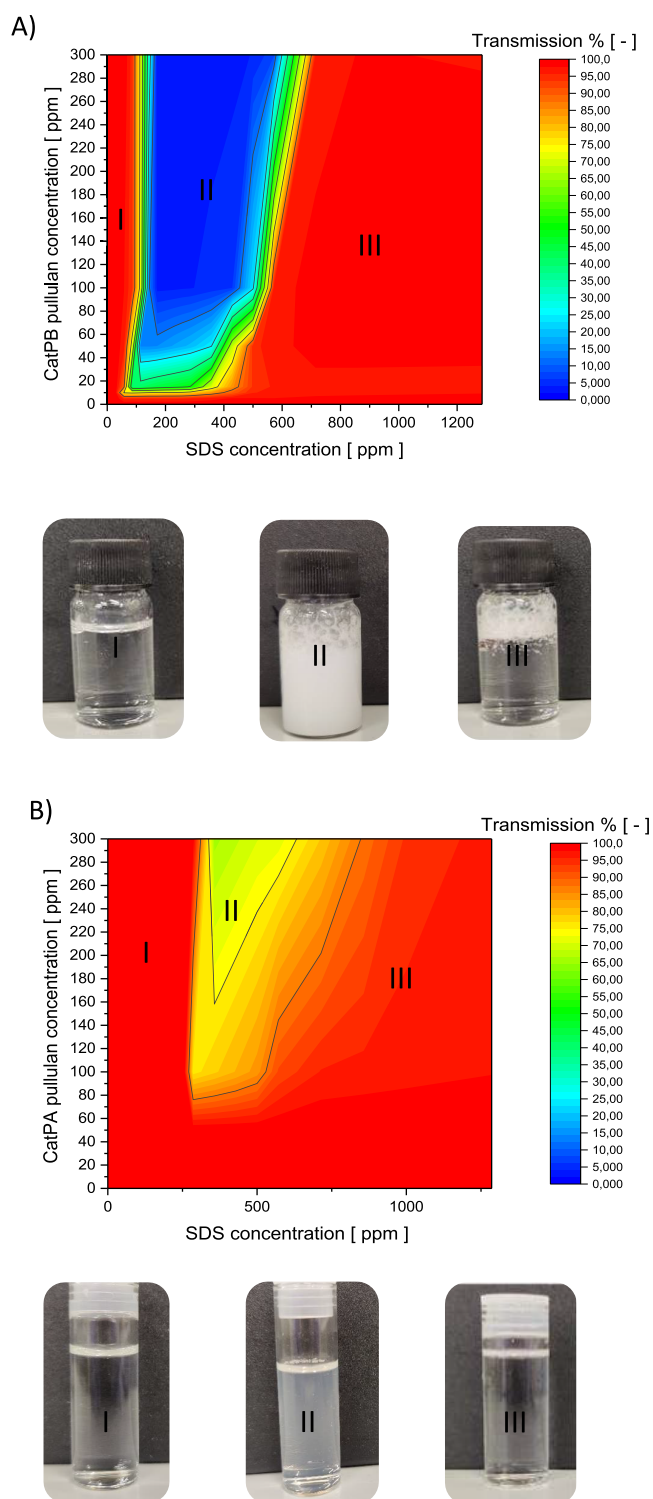
Figure 6. Phase diagram of the **CatPB−SDS** along with pictures of the appearance of polymer−SDS mixtures in the three regions (A). Phase diagram of the **CatPA−SDS** along with pictures of the appearance of polymers−SDS mixtures in the three regions (B).

into insoluble complexes; region III where the complexes are redissolved into a single phase. Likewise, Figure 6B displays the phase diagram for the system **CatPA−SDS**. Even in this case, three separate regions could be observed. Predictively, region 2 was shorter in length than that registered for the **CatPB−SDS** system on account of the lower DS of **CatPA**. Interestingly, at

low **CatPA** concentration (0−70 ppm), no phase separation occurred irrespective of the SDS content. This is again a consequence of the low amount of cationic appendages grafted onto the **CatPA** backbone. Despite showing a different coacervation behavior, **CatPA** and **CatPB** exhibited similar softening properties, as revealed by the secant modulus of polycotton garments treated with these polymers. We can speculate that this result might be a consequence of similar levels of deposition. Overall, UV−visible absorbance results reported in the pseudo phase diagrams allowed to explore the outcome of the interactions between **CatPs** and **SDS** providing a practical tool to rationalize the antiredeposition performance.

■ CONCLUSIONS

This work explored the potential of pullulan derivatives as softening and cleaning aids in a laundry formulation. The grafting of cationic moieties onto the pullulan backbone proved to be essential to increase the softness of the cotton-based fabrics. Interestingly, increasing the level of cationic moieties did not affect fabric softness, suggesting that only a certain amount of cationic appendages is required to drive the adsorption of the polymer onto the fabric surface and thus provide the softening effect. Surprisingly, when compared with a commercially available cationic modified hydroxyethyl cellulose (LR-400), cationic pullulan (CatP) exhibited better antiredeposition performance on all tested textiles, especially on polyester garments that are known to be challenging to clean. To elucidate these results, turbidity measurements were performed, revealing a better capacity of CatPs to stabilize particulate soil suspensions in the presence of surfactants. We speculate that this is the result of a combination of two phenomena, i.e., the coacervate formation of LR-400 with anionic surfactants and its tendency to act as flocculant.

UV−visible absorbance was used to further explore the solution behavior of CatPs in the presence of either a model laundry detergent formulation or a single anionic surfactant (sodium dodecyl sulfate). Results revealed that, driven by electrostatic interaction, CatPs associate with anionic surfactants, forming insoluble complexes and thus leading to an observable phase separation. This phenomenon was monitored by opportunity in adjusting the level of both CatPs and surfactants in solution. The obtained results were used to build SDS-CatPs pseudo phase diagrams. These revealed that the solution behavior of the studied cationic polyelectrolyte in the presence of oppositely charged surfactants is strongly dependent on the polymer architecture and concentration. These findings provide a better understanding of the relation between polymer composition and their macroscopic properties, thus leading the way for the design of novel functional materials for textile conditioning applications.

■ AUTHOR INFORMATION

Corresponding Author

   David A. Fulton − *Chemistry-School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne NE1 8QB, United Kingdom;* orcid.org/0000-0001-8698-0895; Email: david.fulton@ncl.ac.uk

Authors

   Marcellino D'Avino − *Chemistry-School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne NE1 8QB, United Kingdom*

Ruth Chilton − *The Procter & Gamble Company, Newcastle Innovation Centre, Newcastle upon Tyne NE12 9TS, United Kingdom*

Gang Si − *The Procter & Gamble Company, Newcastle Innovation Centre, Newcastle upon Tyne NE12 9TS, United Kingdom*

Mark R. Sivik − *The Procter & Gamble Company, Fabric & Home Care Innovation Centre, Cincinnati, Ohio 45202, United States*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.iecr.3c03552

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Crutzen, A. Fabric Softeners. In *Liquid Detergents*, 2nd edition; Taylor & Francis Group, 2005; vol 129, pp 487−554.

(2) Murphy, D. S. Fabric Softener Technology: A Review. *J. Surfactants Deterg.* **2015**, *18* (2), 199−204.

(3) Levinson, M. I. Rinse-added fabric softener technology at the close of the twentieth century. *J. Surfactants Deterg.* **1999**, *2* (2), 223−235.

(4) Gray, P. G. Liquid laundry detergents containing cationic hydroxyethyl cellulose polymer. WO 2007120547 A1, 2009.

(5) Oikonomou, E. K.; Christov, N.; Cristobal, G.; Bourgaux, C.; Heux, L.; Boucenna, I.; Berret, J. F. Design of eco-friendly fabric softeners: Structure, rheology and interaction with cellulose nano-crystals. *J. Colloid Interface Sci.* **2018**, *525*, 206−215.

(6) McLntyre, D. D.; Calgary, H. J. V. Structural Studies of Pullulan by Nuclear Magnetic Resonance Spectroscopy. *Stärke.* **1993**, *45* (11), 406−410.

(7) Huisinga, L. R. Investigation of the Interactions of Cationic Polyelectrolytes with Anionic Surfactants: Effects of Polymer, Surfactant and Solution Properties. Ph.D. Dissertation, The University of Southern Mississippi: Hattiesburg, MS, 2008. https://aquila.usm.edu/cgi/viewcontent.cgi?referer=&httpsredir=1&article=2175&context=dissertations (accessed August 2023).

(8) Sivik, M. R.; Fliter, K. K.; Fairweather, N. T.; Si, G.; Good, D.; Lu, D.; Qiu, W. Laundry care or dish care composition comprising a poly alpha-1,6-glucan derivative. US 20210395648 A1.

(9) D'Avino, M.; Chilton, R.; Gang, S.; Sivik, M. R.; Fulton, D. A. Evaluating the Role of Hydrophobic and Cationic Appendages on the Laundry Performance of Modified Hydroxyethyl Celluloses. *Ind. Eng. Chem. Res.* **2022**, *61* (38), 14159−14172.

(10) The formulaction, turbiscan stability index (TSI). https://www.formulaction.com/en/knowledge-center/turbiscan-stability-index (accessed April 2023).

(11) Schubert, B. A.; Zannoni, L. A.; Mc Cahin, R. J. Amino modified hydrocarbons. US 20190010257 A1, 2016.

(12) Moraes, F. C.; Antunes, J. C.; Forero Ramirez, L. M.; Aprile, P.; Franck, G.; Chauvierre, C.; Chaubet, F.; Letourneur, D. Synthesis of cationic quaternized pullulan derivatives for miRNA delivery. *Int. J. Pharm.* **2020**, *577*, No. 119041.

(13) Dionísio, M.; Braz, L.; Corvo, M.; Lourenço, J. P.; Grenha, A.; Rosa da Costa, A. M. Charged pullulan derivatives for the development of nanocarriers by polyelectrolyte complexation. *Int. J. Biol. Macromol.* **2016**, *86*, 129−138.

(14) Gabriel, L.; Heinze, T. Structure design of polysaccharides − Chemoselective sulfoethylation of chitosan. *Eur. Polym. J.* **2020**, *140*, No. 109978.

(15) Rathinamoorthy, R.; Gayathri Shree, K.; Vaijayanthi, R.; Brindha, M.; Narmatha, A. Effect of rinse cycle softener treatment on the low-stress mechanical properties of cotton-woven fabric. *Res. J. Text. Appar.* **2020**, *24* (3), 199−210.

(16) Kawabata, S. *The Standardization and Analysis of Hand Evaluation*; Textile Machinery Society of Japan, 1980.

(17) Valentino, P.; Sgambitterra, E.; Furgiuele, F.; Romano, M.; Ehrlich, I.; Gebbeken, N. Mechanical characterization of basalt woven fabric composites: numerical and experimental investigation. *Frat. ed Integrita Strutt.* **2014**, *8* (28), 1−11.

(18) Shakyawar, D. B.; Behera, B. K. *Influence of softening treatments on hand value of woven fabrics produced from Indian wool and their blends*, 2009; 2009.

(19) Golas, P.; Zhou, S.; Xu, C.; Wang, J.; Batteas, J.; Kreeger, L. Phase Behavior of Cationic Hydroxyethyl Cellulose−Sodium Dodecyl Sulfate Mixtures: Effects of Molecular Weight and Ethylene Oxide Side Chain Length of Polymers. *Langmuir.* **2004**, *20* (20), 8482−8489.

(20) Tan, J. J.; Gjerde, N.; Del Giudice, A.; Knudsen, K. D.; Galatini, L.; Du, G.; Schillén, K.; Sande, S. A.; Nyström, B. Interactions in Aqueous Mixtures of Cationic Hydroxyethyl Cellulose and Different Anionic Bile Salts. *J. Agric. Food Chem.* **2023**, *71* (8), 3732−3741.

(21) Gregory, J. Rates of flocculation of latex particles by cationic polymers. *J. Colloid Interface Sci.* **1973**, *42* (2), 448−456.

(22) Dan, A.; Ghosh, S.; Moulik, S. P. Interaction of cationic hydroxyethylcellulose (JR400) and cationic hydrophobically modified hydroxyethylcellulose (LM200) with the amino-acid based anionic amphiphile Sodium N-Dodecanoyl Sarcosinate (SDDS) in aqueous medium. *Carbohydr. Polym.* **2010**, *80* (1), 44−52.

(23) Li, D.; Kelkar, M. S.; Wagner, N. J. Phase Behavior and Molecular Thermodynamics of Coacervation in Oppositely Charged Polyelectrolyte/Surfactant Systems: A Cationic Polymer JR 400 and Anionic Surfactant SDS Mixture. *Langmuir.* **2012**, *28* (28), 10348−10362.

(24) Kayitmazer, A. B.; Koksal, A. F.; Kilic Iyilik, E. Complex coacervation of hyaluronic acid and chitosan: effects of pH, ionic strength, charge density, chain length and the charge ratio. *Soft Matter.* **2015**, *11* (44), 8605−8612.