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“Precipitation morphology and properties of surfactant-polymer complex formed by two cationic polymers.”

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1. Introduction

The combination of surfactants and polymers plays a crucial role in creating product functionality in the personal care field, including cosmetics, pharmaceuticals, and foods, because they can adopt a wide range of complex states, each exhibiting distinct appearances and physical properties. When oppositely charged surfactants and polymers coexist in solution, the complexes exhibit three different dissolved states depending on the stoichiometric ratio of surfactant to polymer (S/P), where S is the number of surfactant ions and P is the number of ionized groups on the polymer (Figure 1) [1–3]. The first state (Stage 1) occurs at $S/P < 1$, where the surfactant concentration is below the critical micelle concentration (CMC), and surfactant ions cooperatively bind to the polar groups of the polymer. The mixed solution remains a single phase, and the complexes retain the polymer's cationic charge. The onset of the second state (Stage 2) is triggered by charge neutralization ($S/P = 1$), leading to the formation of insoluble complexes that precipitate around the isoelectric point. This stage is known as the coacervation region or complex precipitation (CP) region. As the surfactant concentration increases ($S/P > 1$, Stage 3), micelles gradually form on the precipitated complexes, and the complexes eventually re-dissolve, coexisting with free micelles.

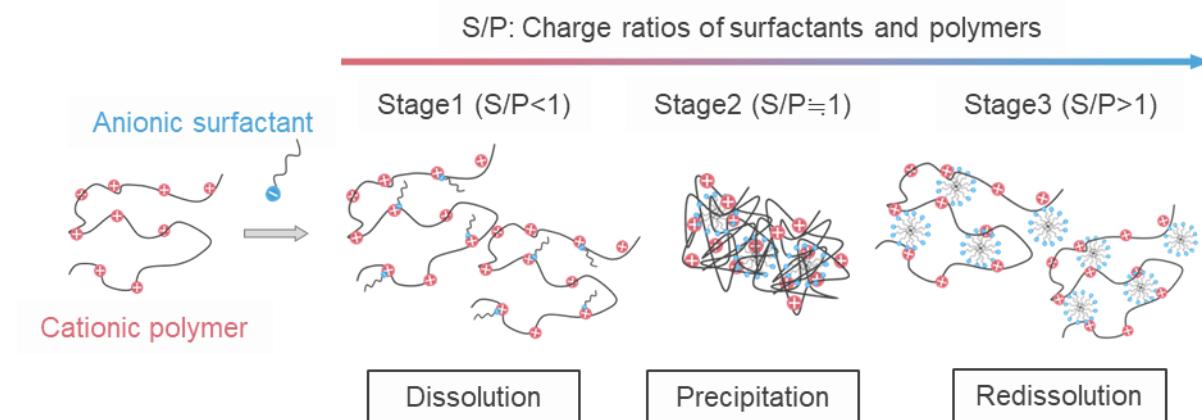


Figure 1. Schematic illustration of the three dissolved states of oppositely charged surfactant/polymer complexes in solution.

Modern conditioning shampoos and body washes containing cationic polymers are examples of mixed solutions in Stage 3. They operate on a mechanism where the complexes undergo coacervation through the dilution of the composition during the washing and rinsing process, transitioning from Stage 3 to Stage 2. The precipitated complexes are adsorbed onto hair and skin, significantly influencing the texture during rinsing and the final feel after drying, both of which are directly perceived by consumers [4–6]. Recently, it has been reported that depending on the molecular structure and concentration of surfactants and polymers, the complexes exhibit different aggregation properties and affect the texture during rinsing [6,7]. For example, Cationic cellulose (CC) is a polymer with low density of cationic groups and high rigidity of the main chain. We have found it to be highly hydrophilic, forming a loose network of complexes and producing a slimy texture (Figure 2(a)). On the other hand, polydiallyldimethylammonium chloride (PDADMAC) is a polymer with high cationic group density and high main chain flexibility. We have found it to be highly hydrophobic, forming strongly aggregated granular complexes and producing a squeaky texture (Figure 2(b)). Thus, depending on the cationic charge and the bendability of the main chain, the precipitation morphology and physical properties of the complexes change, resulting in different textures on the skin. The present study aims to clarify the changes in texture and complex properties when two cationic polymers are combined, and we report on the changes in precipitation morphology and properties of complex containing CC/PDADMAC.

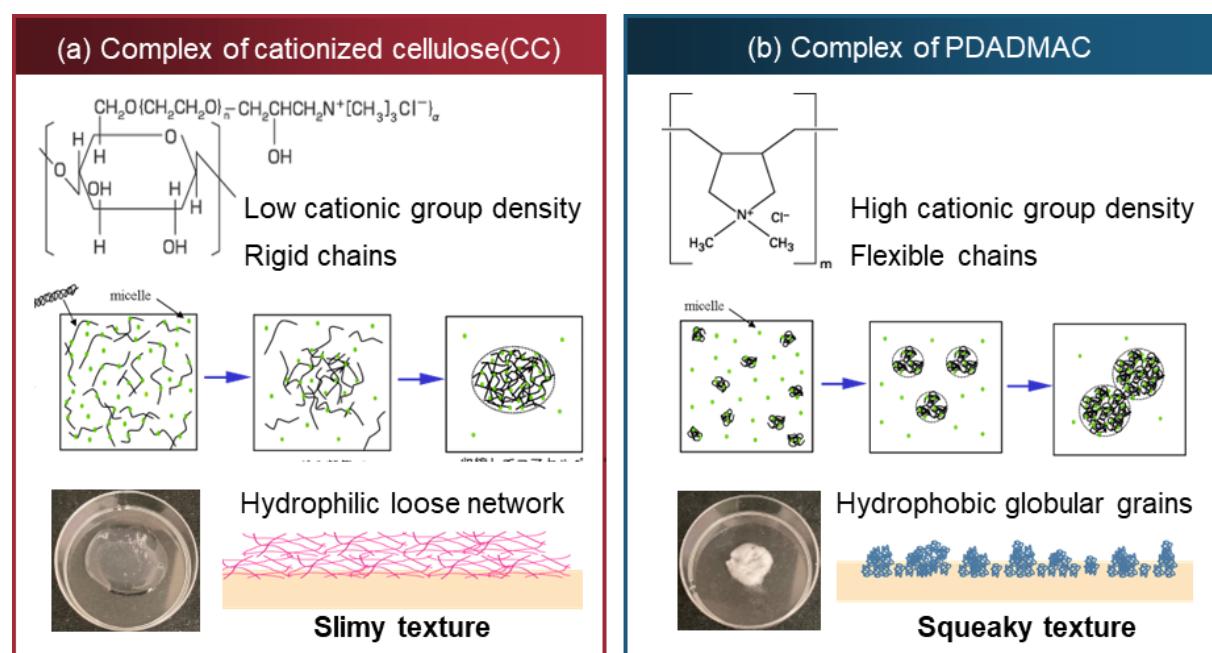


Figure 2. Molecular structure of polymers (a)CC and (b)PDADMAC, appearance and rinsing texture of precipitated complexes.

2. Materials and Methods

2-1. Preparation of materials

Potassium Cocoyl Glycinate was used as an anionic surfactant, Lauramidopropyl Betaine as an amphoteric surfactant, and CC and PDADMAC as cationic polymers. Sample solutions were prepared by mixing each ingredient at predetermined concentrations (Table 1). The fluorescent dyes used in the observation of complex precipitation morphology were fat-soluble Perylene for staining micelles and Cholera Toxin Subunit B Alexa FluorTM555 Conjugate for staining the sugar chains of cationized cellulose.

Table 1. Composition of sample solution.

Sample	Anionic surfactant	Amphoteric surfactant	Cationic Polymer
	10 wt%	10 wt%	0.5 wt%
①CC alone			CC
②PDADMAC alone		Lauramidopropyl Betaine	PDADMAC
③CC/PDADMAC mix	Potassium Cocoyl Glycinate		CC/PDADMAC

2-2. Evaluation of physical properties and Observation of complex

We identified the textures during rinsing and drying by washing the forearm skin with the sample solutions. The precipitated complex was collected through suction filtration of the 5-fold diluted sample solution and observed for its appearance.

2-3. Evaluation of physical properties of complex

Tribological properties of precipitated complexes obtained by 5-fold dilution of the sample solution were measured by installing tribocell on a stress-controlled rotational rheometer. With the precipitated complexes placed in the cell, the kinetic friction coefficient of the complexes was measured at a load of 1 N and the range of 0.00001~1000 mm/s sliding velocity.

The tackiness of the precipitated complex after towel-drying was measured using a static dynamic friction measuring device, with the driving unit reconfigured to a tackiness measuring unit with a vertical movement of the measuring section. The adherent complex was prepared by adding 5 mL of a 5-fold diluted sample solution to a plastic Petri dish, allowing it to stand for 10 minutes, removing the supernatant, adding 5 mL of water, gently shaking, removing the supernatant again, and finally wiping off any residual material with a tissue. The vertical movement was repeated 180 times at a movement distance of 2 mm and a movement speed of 10 mm/s to evaluate the peeling force after the tactile contactor and sample surface adhered to each other. This repetition of the up-and-down movement took 120 seconds, allowing us to track changes in the drying process.

The viscoelasticity of the precipitated complex itself, which was obtained by diluting the model composition 5 times, was measured with a stress-controlled rotational rheometer, and that of the adsorbed complex was measured with a Nano indenter. In the viscoelasticity measurement of the precipitated complex, a parallel plate was used as a jig, the shear strain was fixed at 0.1%, and frequency dispersion measurements were performed to evaluate the storage modulus G' and loss modulus G''. In the viscoelasticity measurement of the adsorption complex, a flat punch indenter (100 µm) and a frequency of 10 Hz were used to evaluate tanδ.

2-4. Observation of complex morphology

An appropriate amount of perylene was added to the model composition, then heated and stirred at 70–80 °C. The mixture was subsequently left to stand to allow the insoluble perylene to precipitate. The supernatant was used as the perylene solubilized model composition. A 5-fold diluted solution of the model composition was dropped 200 µL into the bottom of a glass bottom dish, allowed to stand for 10 minutes, and then the supernatant solution was removed and the morphology of the adhered complex was observed under a fluorescence microscope. In addition, to confirm the coexistence of CC in the complex, 20 µL of CTB555 solution (20 µg/mL) was added to the complex attached to the bottom of the dish, and after 10 minutes of standing, the staining solution was removed, rinsed three times with 200 µL of water, and the supernatant was removed before double-staining images were observed.

3. Results

3-1. Appearance and texture of the complex

Table 2 shows the appearance of the precipitated complex of each sample and its texture during the rinsing and drying process. The CC alone sample formed a gel-like complex that felt slimy upon rinsing and was sticky during the drying process; the PDADMAC alone sample was a resin/wax-like complex that felt squeaky upon rinsing and was sticky during the drying process; the CC/PDADMAC mixture was found to be paste-like, smooth upon rinsing, and non-sticky during the drying process.

Table 2. Appearance and texture of the complex

Sample	Appearance	Rinse feeling	Feeling of dry process
①CC alone		slippery	sticky
②PDADMAC alone		squeaky	sticky
③CC/PDADMAC mix		smooth	non-sticky

3-2. Frictional and adhesive properties of the complex

In texture evaluation, we feel skin friction when we touch and rub our skin with our fingers or palms [8]. Upon application of a product to the skin, it is necessary to consider both frictional and lubricative properties, including the interactions between the skin surface and the product's constituent ingredients. During the application of a skin care cream, the rubbing action occurs at a sliding speed of 10 to several hundred mm/s. It has been reported that there is a correlation between the friction coefficient in this range and textures such as "smoothness" and "stickiness." Therefore, we measured the friction coefficient of the complex precipitated at a 5-fold dilution in the early stages of rinsing over a wide range of sliding speeds (0.00001 to 1000 mm/s) (Figure 3(a)). Comparison of the coefficient of kinetic friction against sliding velocity revealed that the PDADMAC alone sample had a high friction coefficient in the 10-100 mm/s range, corresponding to the speed at which the hand slides across the skin during rinsing, suggesting that this leads to a creaking sensation. On the other hand, the CC alone sample, which had a smooth rinsing texture, showed a low friction coefficient in all regions; the CC/PDADMAC mixture also showed a low coefficient of friction, similar to that of CC. Figure 3(b) shows the time course of the adhesive force of the complex. We observed a change in adhesive strength over 120 seconds, as a general towel-drying guideline. Compared to the CC alone and PDADMAC alone samples, which exhibited high adhesive strength during the drying process, the CC/PDADMAC mixed sample was found to exhibit lower adhesive strength.

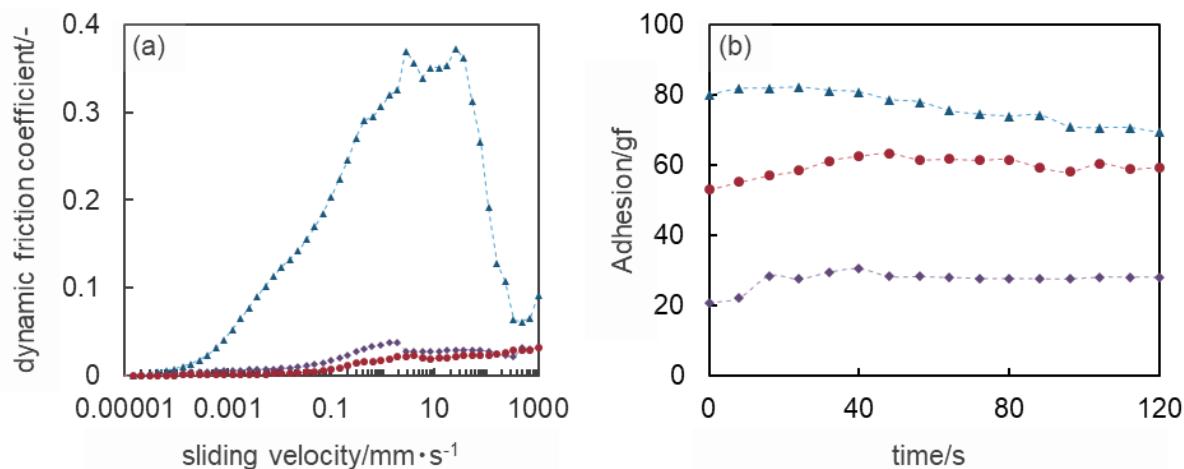


Figure 3. (a) Coefficient of kinetic friction and (b) adhesion of complex (●CC, ▲PDADMAC, ♦CC/DADMAC)

3-3. Viscoelastic properties of the complex

Figure 4(a) shows the change in storage modulus G' and loss modulus G'' of the complex versus angular frequency; the PDADMAC alone sample exhibits high G' and strong solid-like properties, while the CC/PDADMAC mixture sample has a lower G' than the PDADMAC alone sample. G' is lower, suggesting that the change in rheological properties suppressed the secondary aggregation of PDADMAC. The viscoelastic properties of the complexes adsorbed on the skin when wet were evaluated by nanoindentation measurements (Figure 4(b)). Comparison of the loss tangent tanδ revealed that the complex of CC alone sample has a tanδ>1, indicating a viscous dominant property, whereas the PDADMAC alone sample has an elastic dominant property with tanδ=0.19. Meanwhile, the CC/PDADMAC mixed sample was found to have intermediate properties between the two with tanδ=0.91.

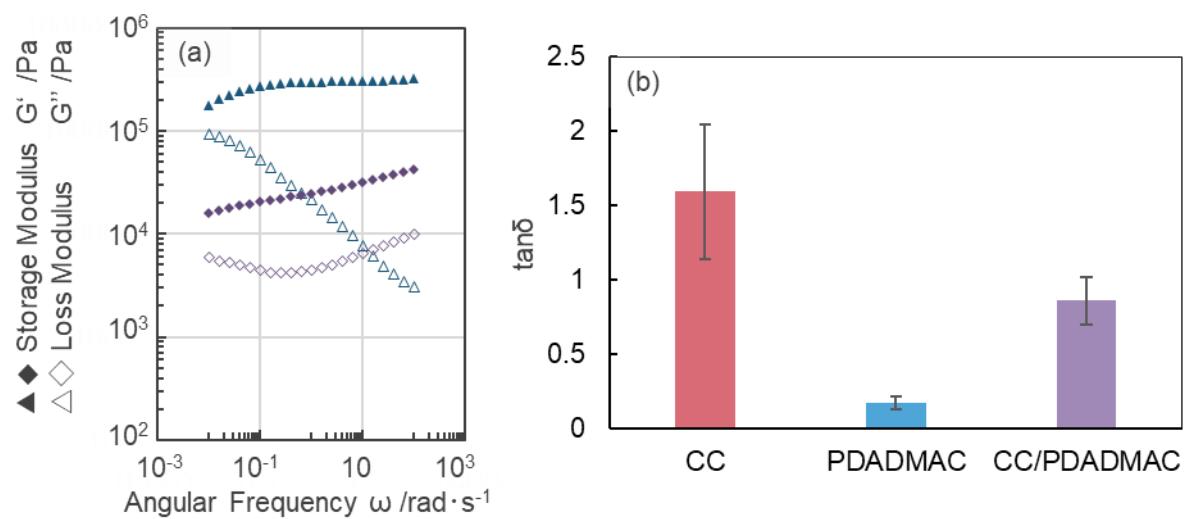


Figure 4. Viscoelastic properties of (a) precipitation complexes (PDADMAC: ▲ , CC/PDADMAC : ◆) and (b) adsorption complexes

3-4. Morphological observation of the complex

Figure 5 shows fluorescence images of the precipitation morphology of the complex for each sample observed with a confocal laser microscope. The fluorescent dye, perylene, is solubilized in the micelles of the complexes. In the CC alone sample, the spreading of the network complex was observed, while in the PDADMAC alone sample, granular particles of several μm in size were observed spreading all over the surface. In the CC/PDAMDAC mixture sample, a mixture of network and granular complexes was locally observed. It was assumed that the granular complexes of PDADMAC were entrapped within the network-like complexes of CC. This mixed adsorption was confirmed through double staining of CC and PDADMAC, allowing their positions to be verified. Figure 5(d) shows the fluorescent image of the double staining. The blue area is the CC and PDADMAC complex, and the pink area is CC. The blue area without red, indicated by the yellow arrow, is the PDADMAC complex only. Compared to the PDADMAC-only sample, the PDADMAC complex is incorporated into the gel network of the CC complex to suppress secondary aggregation.

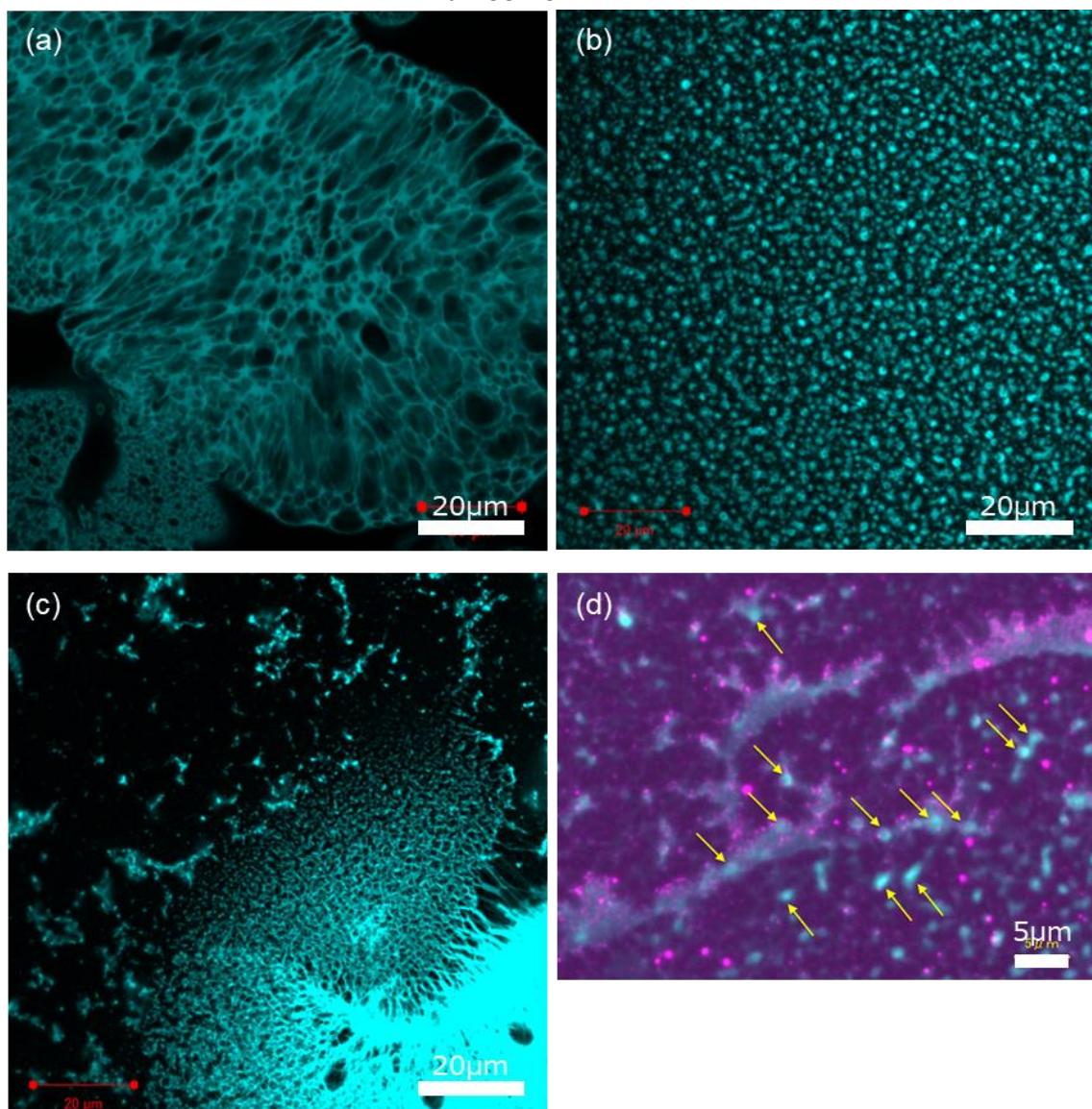


Figure 5. Fluorescent images of complex precipitation morphology ((a) CC, (b) PDADMAC, (c) CC/PDADMAC) and (d) Double stained image of CC/PDADMAC (yellow arrows point to complexes formed by DADMAC only).

4. Discussion

The higher the density of cationic groups in a polymer, the more crosslinking points are formed through electrostatic interactions with surfactant micelles, which leads to stronger complex aggregation [7]. Therefore, when CC, which has a low cationic group density, and PDADMAC, which has a high cationic group density, are mixed, it is thought that they form a characteristic mixed complex that combines the properties of both. Figure 6 shows an image of the precipitation process of a CC/PDADMAC mixture. Before dilution, CC and PDADMAC are uniformly dissolved, but when the polymer micelles decrease due to dilution, crosslinking between the polymers begins. At this time, aggregation and precipitation of the PDADMAC complex, which has high cohesive force, begins, and polymer crosslinking with the CC complex via micelles also progresses with the PDADMAC complex as a nucleus. As dilution progresses, the polymer-crosslinked PDADMAC and CC complexes aggregate and shrink. In this way, it is thought that intermolecular crosslinking between the CC complex and the PDADMAC complex via micelles progresses, and a localized gel network of the CC complex containing the PDADMAC complex is precipitated. As a result, the secondary aggregation of PDADMAC is alleviated by the gel network of CC, forming a softer complex than PDADMAC, which reduces the squeaky feeling during rinsing and shows a smooth texture. Additionally, the local complex formation with the primary aggregate particles of PDADMAC as the nucleus reduces the adhesive strength, which reduces the sticky feeling during the drying process. In the future, we believe that by combining cationic polymers with different cationic group densities in various ratios, it will be possible to apply this technology to the formulation design that allows flexible control of the texture from the washing process to the drying process of body soap and shampoo.

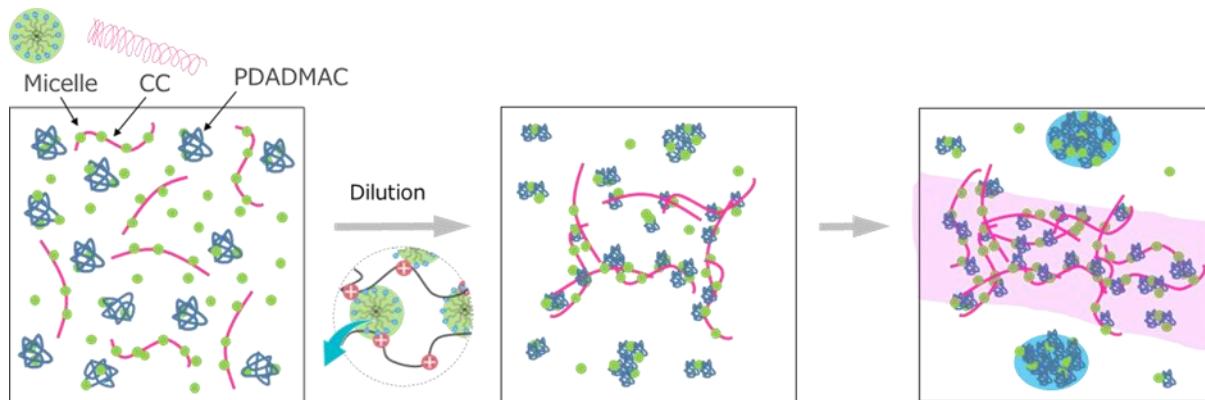


Figure 6. Schematic illustration of the precipitation process of CC/PDADMAC mixture

5. Conclusion

We discovered that mixing CC, which has a low cationic group density and high main chain rigidity, with PDADMAC, characterized by a high cationic group density and low main chain rigidity, creates a mixed complex with intermediate viscoelastic properties and unique adhesive qualities. This combination results in a smooth rinsing texture and a non-sticky feel during the drying process, which cannot be achieved with just CC or PDADMAC alone. This is because the incorporation of the PDADMAC complex into the CC complex gel network proceeds with the PDADMAC complex primary particles as the nucleus, suppressing the secondary aggregation of PDADMAC.

6. Reference

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