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Light-Triggered Rheological Changes in a System of Cationic Wormlike Micelles Formulated with a Photoacid Generator

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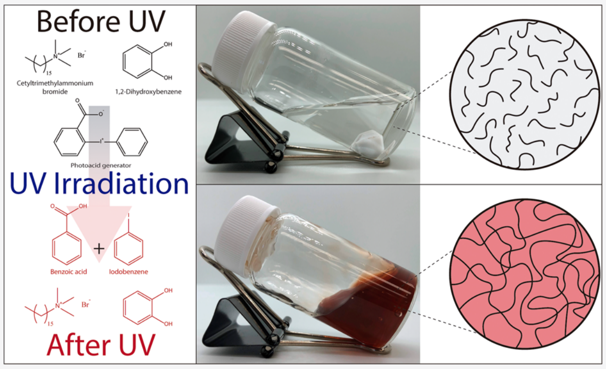
ABSTRACT: "Smart" fluids displaying large changes in their rheological properties in response to external stimuli have been of great interest in recent years. For example, "smart" wormlike micelles (WLMs) that respond to pH can be readily formulated by combining a cationic surfactant such as cetyltrimethylammonium bromide (CTAB) with an aromatic compound such as 1,2-dihydroxybenzene (DHB). Here, we show that a pH-responsive aqueous formulation as mentioned above can be simultaneously made responsive to ultraviolet (UV) light by incorporating a photoacid generator (PAG) into the system. A commercially available PAG, diphenyliodonium-2-carboxylate, is used here. Upon exposure to UV light, this PAG irreversibly photolyzes into iodobenzene (IB) and benzoic acid (BA), with the formation of BA, leading to a drop in pH. WLMs formed by mixtures of CTAB, DHB, and the PAG are systematically characterized before and after UV irradiation. As the PAG photolyzes, an increase in the viscosity of WLMs occurs by a factor of 1000. We show that the ratio of the zero-shear viscosity η_0 (after UV/before UV) depends on the initial pH of the sample. The UV-induced increase in η_0 can be attributed to the growth of WLMs in solution, which in turn is influenced by both the ionization state of DHB and the presence of IB and BA.



1. INTRODUCTION

In the preface of the book *Smart Wormlike Micelles—Design, Characteristics and Applications*,[1] the authors state: "Can you imagine water being thickened into a highly viscoelastic gel upon dissolving just one drop of detergent inside?", and a little further on, "Now imagine this elastic gel being illuminated by ultraviolet (UV) light ... and suddenly it reverts back to water?". Indeed, all of this is possible under conditions where the detergent (surfactant) molecules aggregate into long chains, called wormlike micelles (WLMs), and the chains then get broken into shorter units upon shining UV light.

Surfactants are amphiphilic molecules that can self-assemble in solution into different types of aggregates such as spherical micelles,[2] WLMs,[3−5] hexagonal phases,[6] lamellae,[7] vesicles,[8] and others.[9−11] The structure of the aggregate can be rationalized by considering the geometry of the surfactant molecule in terms of the critical packing parameter (CPP).[12] This CPP depends on the molecular identity of the surfactant, the presence of salt or some specific cosolutes, temperature, concentration, ionic strength, and so on. WLMs are a special type of aggregate—they are long chains[13,14] that can reach thousands of nanometers in length.[15] Because the chains are long and polymer-like, solutions of WLMs exhibit viscoelastic properties. Because of these viscoelastic properties, WLMs find application as drag reducing agents, in enhanced oil recovery, in home and personal care products, and more.[16−18]

More interestingly, WLMs can be made responsive to external stimuli such as light,[19−24] temperature,[23,25,26] pH,[23,27−31] CO_2,[21,32−34] redox reaction,[35,36] and even a combination of stimuli.[21,23,37] These systems, called "smart" WLMs,[38] have a common feature in that the stimulus causes a drastic change in the size (contour length) of the WLM chains. In turn, the rheological properties of the WLM solution such as its zero-shear viscosity (η_0) or its relaxation time (τ_R) can be varied by orders of magnitude. This ability to modulate the rheology by external stimuli further expands the applicability of smart WLMs.

Among the various stimuli, solution pH has been the most studied. There are several studies describing smart WLMs that are responsive to pH. The various strategies in these studies include the use of a pH-responsive surfactant,[21,28,29] the combination of a conventional surfactant and a pH-responsive organic compound such as oxalic acid,[28] hydroxycinnamic acid,[22] or benzenedioic acid,[31] and the incorporation of

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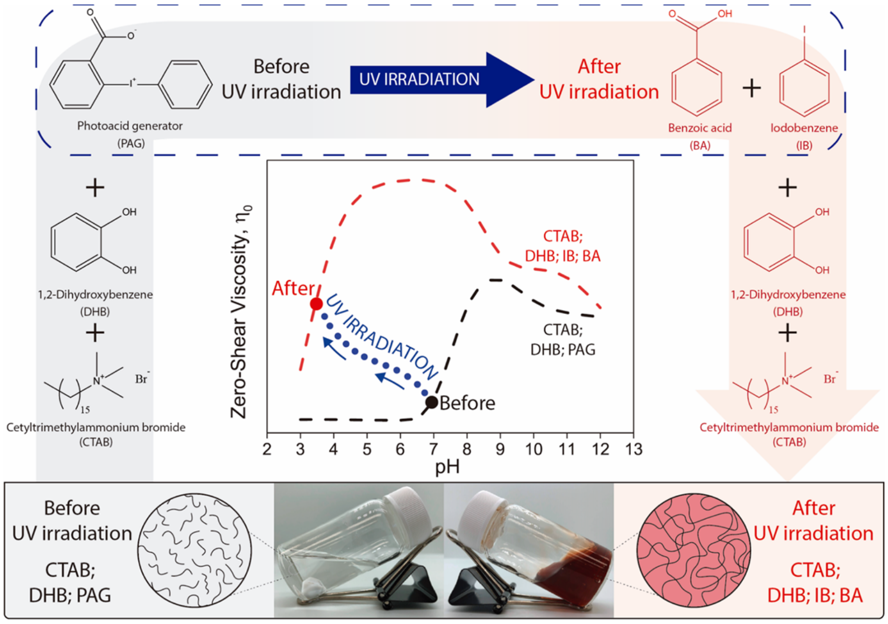

Figure 1. Schematic representation of the system and the concept behind the work. The center graph shows the zero-shear viscosity η_0 as a function of solution pH for two cases. The black line represents the solution containing CTAB, DHB, and the PAG (structures in the top left). The red line represents the solution containing CTAB, DHB, IB, and BA. As shown by the reaction on the right, IB and BA are the products formed by the UV-induced photolysis of the PAG. The blue line represents the change in η_0 and pH due to UV irradiation of the sample at pH 7. As the pH drops to ~3.5, the viscosity increases 1000-fold. The bottom panel shows visual evidence for this viscosity change: initially (left), the sample is colorless and has a viscosity close to water, whereas after UV irradiation, the sample is much more viscous and has a reddish color. The sample contains [CTAB] = [DHB] = 50 mM and [PAG] = 10 mM.

CO_2.[21,32−34] It is possible to formulate pH-responsive WLMs that can be triggered over any pH range—acidic,[30,39] neutral,[23] or basic.[40,41] WLMs that are responsive under acidic conditions are particularly attractive as they could have an important application in oil recovery (acid diversion in carbonate rocks).[17,42]

Light as a stimulus to trigger changes in WLMs is advantageous in many ways. Compared to other stimuli, light is noninvasive and can be introduced without affecting the sample composition. Light sources are readily available, and light can be directed at a precise spatial location and at a chosen point in time. WLMs that respond to light have been created by exploiting light-induced changes in photosensitive molecules such as cis−trans isomerization[15,20,21,24] or dimerization.[43,44] The photosensitive compound can be a surfactant[21,24] or an additive present in the formulation.[15,20,45] Initial studies on light-responsive WLMs required the synthesis of specialized photosensitive molecules such as surfactants with azobenzene units. However, many studies have recently demonstrated the same results with common molecules that are readily available from commercial vendors. For example, we recently showed that a fluid based on two commercially available molecules, a cationic surfactant and an azobenzene-bearing salt, could be cycled using UV and visible light between states that were a million-fold apart in their viscosity.[46]

In this study, we have devised a "smart" WLM formulation that is responsive to both pH and light. The system contains the cationic surfactant cetyltrimethylammonium bromide (CTAB) along with the organic acid 1,2-dihydroxybenzene (DHB). We initially found that mixtures of CTAB and DHB formed WLMs that were responsive to pH. To the above binary mixture, we then added the photoacid generator (PAG) diphenyliodonium-2-carboxylate. As the name indicates, PAGs are compounds that generate acid upon exposure to light (typically in the UV range of wavelengths). We show that adding the above PAG to the CTAB/DHB mixture makes the system sensitive to UV light too. This can be viewed as a general strategy to convert a pH-responsive system to a light-responsive one, and it has been employed before by us and others for the photogelation of fluids containing nanoparticles,[47] biopolymers such as alginate,[48,49] or small-molecule hydrogelators. However, to our knowledge, there have been no reports of PAGs being used to trigger fluids based on WLMs. PAGs are an intriguing class of molecules, and we hope that this work also helps to stimulate further interest in their use in creating new types of "smart" fluids.

2. MATERIALS AND METHODS

2.1. Materials. CTAB, DHB, iodobenzene (IB), benzoic acid (BA), hydrochloric acid, and sodium hydroxide were purchased from Sigma-Aldrich, and PAG and diphenyliodonium-2-carboxylate monohydrate were purchased from TCI Chemicals, all of them with purity higher than 98%. Erucyl bis(hydroxyethyl)methyl ammonium chloride [EHAC, commercial name Ethoquad E/12-75] was received as a gift from Akzo Nobel. The product is supplied as a solution of 75% surfactant in isopropyl alcohol (IPA). IPA was removed in a vacuum oven at room temperature and the surfactant was then freeze-dried overnight before use.

2.2. Sample Preparation and Response to UV Light. All samples were prepared gravimetrically using deionized water, and the pH was adjusted to ±0.1 units using aqueous solutions of sodium hydroxide or hydrochloric acid. Samples were irradiated with UV light from an Oriel 200 W mercury arc lamp. A dichroic beam turner with a mirror reflectance range of 350−450 nm was used to access the UV range of the emitted light. The sample (10 mL) was placed in a 20 mL vial, and irradiation was done for a specific duration (typically 30 min) under mild stirring at 25 °C. Then, 0.5 mL of sample was removed for measuring the rheology. The rest of the sample was then irradiated for a second duration and the above process was repeated. UV−vis spectra (Figure S1) were obtained on a spectrophotometer (Hewlett−Packard, model 8453) for aqueous solutions of PAG or DHB at pH 7.0 and also after irradiating the PAG solution for 2 h.

2.3. Rheology. Steady-shear and oscillatory rheology were conducted on an AR2000 (TA Instruments) and a HAAKE MARS 40 (Thermo Fisher) instrument, respectively. The flow curves (apparent viscosity as a function of shear rate) were obtained using a cone-and-plate geometry (20 mm diameter, 1° cone angle) and the dynamic frequency and stress sweeps using a parallel plate geometry (30 mm diameter plates, 1 mm gap). Stress sweeps were obtained at a fixed frequency of 1 Hz and frequency sweeps at a fixed stress of 1 Pa. The experiments were performed at 25 °C, and before each experiment, the samples were equilibrated for at least 10 min at this temperature.

3. RESULTS AND DISCUSSION

Figure 1 shows the molecules used in this study as well the concept behind the work. We combine 50 mM of the cationic surfactant CTAB with 50 mM of the organic acid DHB and 10 mM of the PAG (diphenyliodonium-2-carboxylate). The black line corresponds to the zero-shear viscosity η_0 of the above solution at different pHs. When this solution is irradiated with UV light, the PAG will be photolyzed by the reaction shown in Figure 1 and will thereby decompose into 10 mM each of BA and IB (UV−vis spectra can be seen in Figure S1). In Figure 1, the red line corresponds to the η_0 at different pHs of a solution containing 50 mM of CTAB and DHB + 10 mM of BA and IB. Conceptually, the red line is the rheology after UV irradiation. Thus, when the CTAB/DHB/PAG sample at pH 7 is exposed to UV light, the pH drops from 7 to about 3.5. Correspondingly, the viscosity increases almost 1000-fold, as shown by the hypothetical path (blue points in Figure 1). Visual inspection also showed that the solution turned reddish, as can be noted from the vials in Figure 1. Note that the changes in viscosity, pH, and color induced by UV light are irreversible. Although the purpose of this figure is to illustrate the concept, the curves in the graph correspond to the actual data on our system, as shown below.

Oscillatory rheology was obtained to confirm that WLM structures are involved in this system. Figure 2 shows the frequency sweep for the solutions containing CTAB + DHB and CTAB + DHB + PAG, both at pH 9.0 and 25 °C. As can be seem, both solutions present the results expected for solutions containing entangled WLMs,[51] where in lower shear frequencies, the solution behaves predominantly viscous (dissipation of the shear stress applied) with $G'' > G'$ and in higher frequencies, predominantly elastic, with $G' > G''$. The inverse of the frequency where $G' = G''$ is defined as the relaxation time,[52] τ_R. As is shown in Figure 2, the addition of PAG into the CTAB + DHB solution affects its rheological behavior, by changing τ_R from 130.0 to 3.10 s. Additionally, the solutions do not behave perfectly as Maxwellian fluids once they did not follow the semicircular shape expected in the graph of $G' \times G''$, as can be seen in Figure S2. Responsiveness to UV light was also investigated by oscillatory rheology using the EHAC + DHB + PAG system, and similar trends shown in Figure 2 were obtained and can be seen in Figure S3.

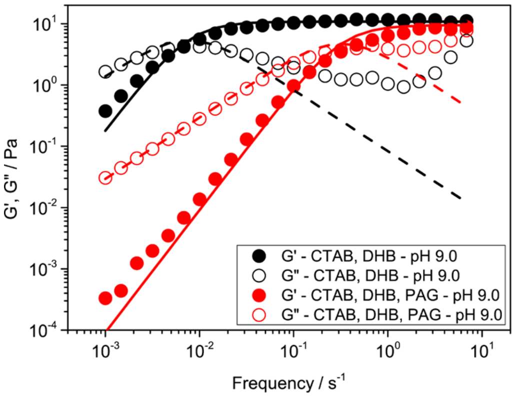

Figure 2. Elastic (G', filled symbols) and viscous (G'', empty symbols) moduli as a function of frequency for the solution containing CTAB + DHB or CTAB + DHB + PAG both at pH 9.0. [EHAC] = [DHB] = 50 mM and [PAG] = 10 mM. The lines correspond to the fits of the Maxwell model.

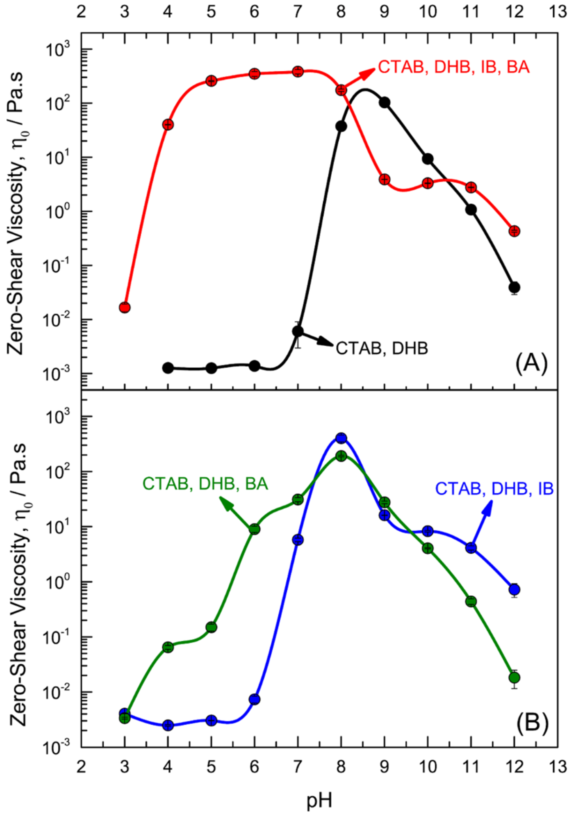

Figure 3. Zero-shear viscosity η_0 as a function of solution pH for mixtures of: (A) CTAB, DHB, IB, and BA (red line); CTAB and DHB (black line); (B) CTAB, DHB, and BA (green line); and CTAB, DHB, and IB (blue line). The following concentrations were used: [CTAB] = [DHB] = 50 mM and [IB] = [BA] = 10 mM. The lines are only guide to the eyes, and the values were obtained from at least a duplicate.

Figure 3 shows rheological data (for η_0, from steady-shear rheology) for various combinations of CTAB (50 mM), DHB (50 mM), IB (10 mM), and BA (10 mM) from pH 3 to 12. All these data are for samples before any UV irradiation. Data for (i) CTAB + DHB and (ii) CTAB + DHB + BA + IB are grouped in Figure 3A. Data for (iii) CTAB + DHB + BA and (iv) CTAB + DHB + IB are shown in Figure 3B. The comparison of the viscosities for all the solutions investigated, without UV irradiation, can be seen in Figure S4 and the flow curves can be seen in Figures S5−S9. In Figure 3A, the CTAB/DHB mixture shows a large increase in viscosity as the pH is increased above 7.0, with η_0 then peaking around a pH of 9.0 and then sharply decreasing. To explain this, we note that

DHB has two pK_a values at 9.45 and 12.8. At low pH (<7), DHB is fully protonated, and the neutral DHB interacts very weakly with the CTAB molecules. With the first deprotonation (at pH > 7), DHB becomes monoanionic, and in this state, it strongly interacts with the cationic CTAB. The aromatic counterion of DHB embeds into the micellar palisade layer (because of its hydrophobicity), and such binding of the counterion strongly attenuates the micellar charge. This enables CTAB to form long WLMs, and the entanglement of these long chains drastically increases the solution viscosity. The drop in η_0 upon further pH increase is explained by the second DHB deprotonation. The dianionic DHB is less likely to remain embedded in CTAB micelles because of its high solubility in water—instead, the DHB unbinds from the micelles. This has the effect of reducing the length of the WLMs and thereby reducing η_0.

The effect of IB or BA (photolysis products of the PAG) on the viscosity of CTAB/DHB was then investigated. IB is an uncharged hydrophobic molecule, and it has negligible effect on η_0 apart from a small increase at high pH (Figure 3B). BA on the other hand is a weak organic acid with a pK_a of 4.2. Figure 3B shows that BA serves to increase η_0 over the pH range of 4−7. In this pH range, DHB is protonated, but BA becomes deprotonated and has low affinity for the micellar palisade.[3,50] Thus, BA induces WLMs of CTAB in this pH range. Surprisingly, the η_0 value for the solution containing all the four components (CTAB, DHB, BA, and IB) is much higher than that with three out of the four components. This indicates an important synergistic enhancement of η_0 when both BA and IB are present. A possible explanation is that the presence of IB and BA changes the chemical potential of DHB so as to favor its insertion into CTAB micelles. As the DHB is fully protonated in this pH range, the electrostatic interactions with CTAB are weak. However, when both BA and IB are present, some of the BA and possibly also some DHB are apparently able to bind to CTAB and thereby induce WLM growth.

Having characterized all the scenarios without UV irradiation, we then added the PAG into the base solution of CTAB and DHB. Prior to UV exposure, the PAG has negligible influence on the CTAB/DHB rheology at pH up to 7 (Figure S10). We then took a sample of CTAB/DHB/PAG at an initial pH of 7.0 and irradiated it with UV light for a period of 30 min. A portion of the sample (0.5 mL) was then removed and its rheology measured under steady shear. Irradiation was continued for the rest of the sample for another 30 min, then a sample was again removed for rheology, and the procedure was repeated for additional intervals of time. In the absence of UV, the photolysis reaction stops, and thus, the rheology that is measured is characteristic of the UV irradiation time. We were thus able to generate the data shown in Figure 4A, which are for the viscosity η versus shear rate after different irradiation times. Over the first 90 min, η increases 10-fold, but the sample continues to show a Newtonian profile (constant η over the range of shear rates). With further irradiation, the rheology becomes noticeably shear-thinning, that is, there is a decrease in η beyond a critical shear rate. The zero-shear viscosity η_0 (i.e., the viscosity in the Newtonian plateau region) rises exponentially with irradiation time and it finally saturates after 390 min, as shown by the semilog plot in Figure 4B (a linear version of this plot, normalized by its initial viscosity, is shown in Figure 6B). The final ratio of η_0 (after UV) to η_0 (before UV) is more than 100.

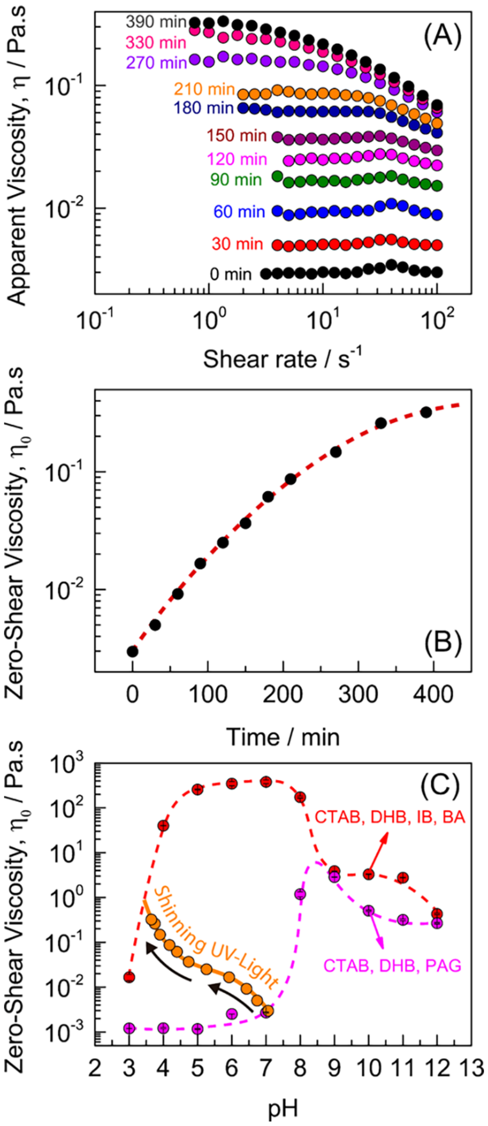

Figure 4. Effect of UV irradiation on the rheology of samples containing CTAB, DHB, and PAG. (A) Flow curves from steady-shear rheology (plots of viscosity η vs shear-rate) of a sample with initial pH 7.0 at various UV irradiation times. (B) Zero-shear viscosity η_0 as a function of irradiation time, extracted from the plots in (A). (C) Data for η_0 vs pH for the UV-irradiated sample at various irradiation times. On this plot, data for η_0 vs pH for a CTAB + DHB + PAG solution and for a CTAB + DHB + IB + BA solution are also plotted for comparison. The concentrations used are [CTAB] = [DHB] = 50 mM and [PAG] = [IB] = [BA] = 10 mM. The lines are only guide to the eyes, and the values were obtained from at least a duplicate.

In addition to rheology, we also monitored the solution pH at various times after UV irradiation. The combined data for η_0 and pH are mapped onto the plot in Figure 4C. This data clearly shows the initial (before UV) and final states of the sample. Initially, the sample contains CTAB, DHB, and PAG, with its initial pH being 7 and its η_0 being low. UV causes the pH to drop and the η_0 to rise. Note that along with the pH drop, the photolysis products (BA and IB) are key to the rise in η_0, as discussed under Figure 3. After 390 min of UV irradiation, the sample pH drops to about 3.5 and the final η_0 reached coincides with the η_0 expected for a mixture of CTAB, DHB, BA, and IB at the same pH in the absence of UV.

Besides, UV caused the CTAB/DHB/PAG sample to transform from clear to a reddish color probably because of some photolysis byproducts. In comparison, CTAB/DHB/BA/IB was colorless below pH 9.0. This shows that the compound giving color to the sample does not significantly affect its viscosity.

The effect of UV light on CTAB/DHB/PAG samples depends on the initial pH, as shown in Figure 5. Here, solutions at pH 7, 8, 9, and 10 are UV-irradiated, and the drop in pH with time is plotted (the data in Figure 5A is normalized by the initial pH and replotted in Figure 5B). The pH decreases at the same rate in all cases over the first 75 min. Thereafter, there is a sharper decrease in pH when the initial pH is 7 (after a pH of 6.2 is reached). These data show that the initial pH of the sample should be carefully chosen to modulate the time-dependent rheology of the sample.

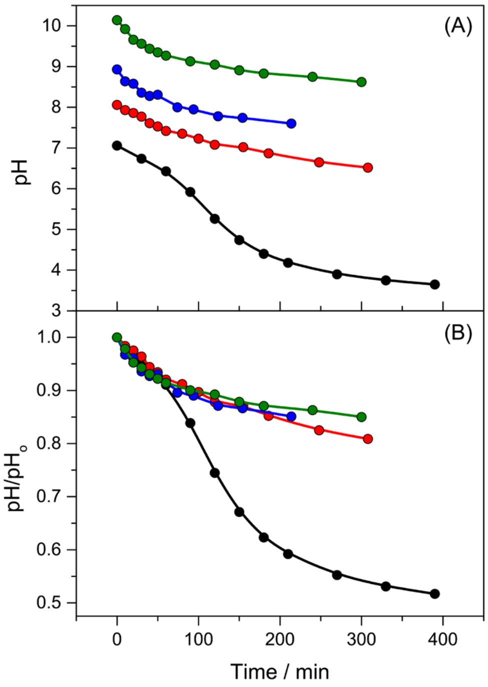

Figure 5. Solution pH as a function of UV irradiation time for the same CTAB/DHB/PAG sample starting at different initial pHs. (A) Raw data and (B) normalized data, where the pH is normalized by the initial pH (pH_0). [CTAB] = [DHB] = 50 mM and [PAG] = 10 mM. The lines are only guide to the eyes.

In order to boost the response, we experimented with a different cationic surfactant. This surfactant, EHAC, has a C_{22} tail in comparison to the C_{16} tail in CTAB. Because of the longer tail, EHAC is a much stronger surfactant—for example, its critical micelle concentration is 50-fold lower than that of CTAB.[46] Results for an EHAC/DHB/PAG sample are compared to those for the CTAB/DHB/PAG one in Figure 6. In both cases, the samples are at pH 7 at t = 0, and thereafter, they are irradiated with UV light. The viscosity rises and the pH decreases with time. For a ready comparison of the two surfactants, the data shown in Figure 6 are normalized by their values at t = 0 (the raw, un-normalized data are provided in Figure S11). The EHAC sample is 100× the viscosity of the CTAB sample at t = 0. Upon UV irradiation, the viscosity and pH change faster for the EHAC sample. The highest η_0 is reached within 180 min of irradiation, and this η_0 is 1000× the value at t = 0. For comparison, in the case of CTAB sample, η_0 rises 100× the initial value and it does so in 390 min. With just 30 min of UV, the pH decreased 0.5 units for both samples, but the corresponding rise in η_0 was 10-fold with EHAC versus just 2-fold for CTAB. These results show that light-induced changes in properties depend on all the components present in the system, including the surfactant. Visual changes in the EHAC sample induced by UV light are shown in Figures S12 and S13.

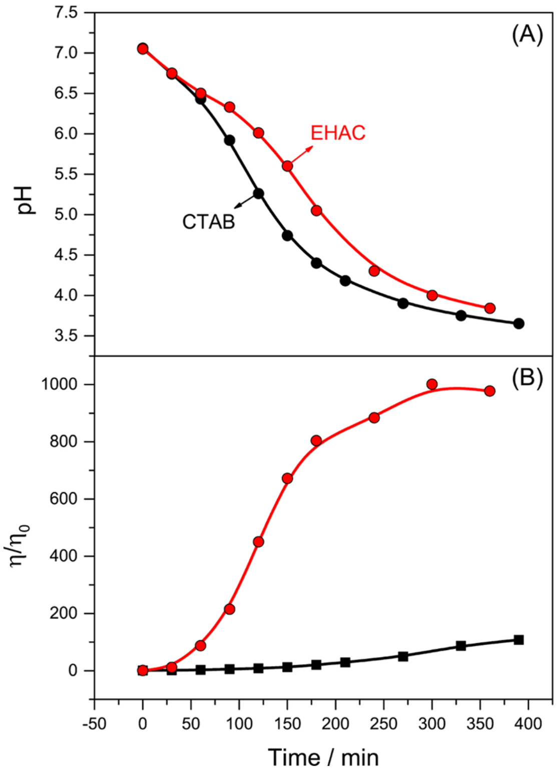

Figure 6. Solution pH (A) and zero-shear viscosity (B) as a function of UV irradiation time for a CTAB/DHB/PAG sample and an EHAC/DHB/PAG sample. Both samples start at a pH of 7. The viscosity data are normalized by its value at t = 0. [CTAB] = [EHAC] = [DHB] = 50 mM; [PAG] = 10 mM for CTAB and 15 mM for EHAC. The lines are only guide to the eyes.

4. CONCLUSIONS

We have devised a surfactant-based fluid whose rheology is sensitive to both pH and UV light. The components of the fluid are a cationic surfactant (CTAB), an aromatic compound (DHB), and a PAG (diphenyliodonium-2-carboxylate). The CTAB/DHB mixture is pH-responsive: its zero-shear viscosity η_0 increases by more than 5 orders of magnitude between a pH of 6 and 9. This rise in η_0 is due to the formation of WLMs, which are induced when one of the carboxylates on DHB is deprotonated. The addition of PAG to the CTAB/DHB mixture makes the fluid responsive to UV light. Upon UV irradiation, the PAG gets photolyzed into BA and IB, and as a result, the solution pH drops from 7 to 3.5 and η_0 rises 100-fold. This viscosity increase mirrors that seen with CTAB/DHB when BA and IB are both added. The extent of viscosity increase depends on the initial pH and the UV irradiation time. A change of surfactant from CTAB to EHAC considerably increases the maximum η_0 after irradiation (a net 1000-fold rise over η_0 before UV), and this higher η_0 is also reached in a shorter UV irradiation time (390 min for CTAB vs 180 min for EHAC). Our study shows that PAGs are a powerful class of molecules that can impart light sensitivity to many kinds of fluids, and the use of PAGs in WLM systems is first reported herein.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.0c01439.

> UV spectra of DHB and PAG aqueous solution; zero-shear viscosity; apparent viscosity as a function of shear rate; influence of PAG in solution viscosity; zero-shear viscosity of the solution containing CTAB or EHAC, DHB, and PAG; and changes on the solution appearance (PDF)

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Notes

The authors declare no competing financial interest.

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Supplementary material for:

Light-Triggered Rheological Changes in a System of Cationic Wormlike Micelles Formulated with a Photoacid Generator

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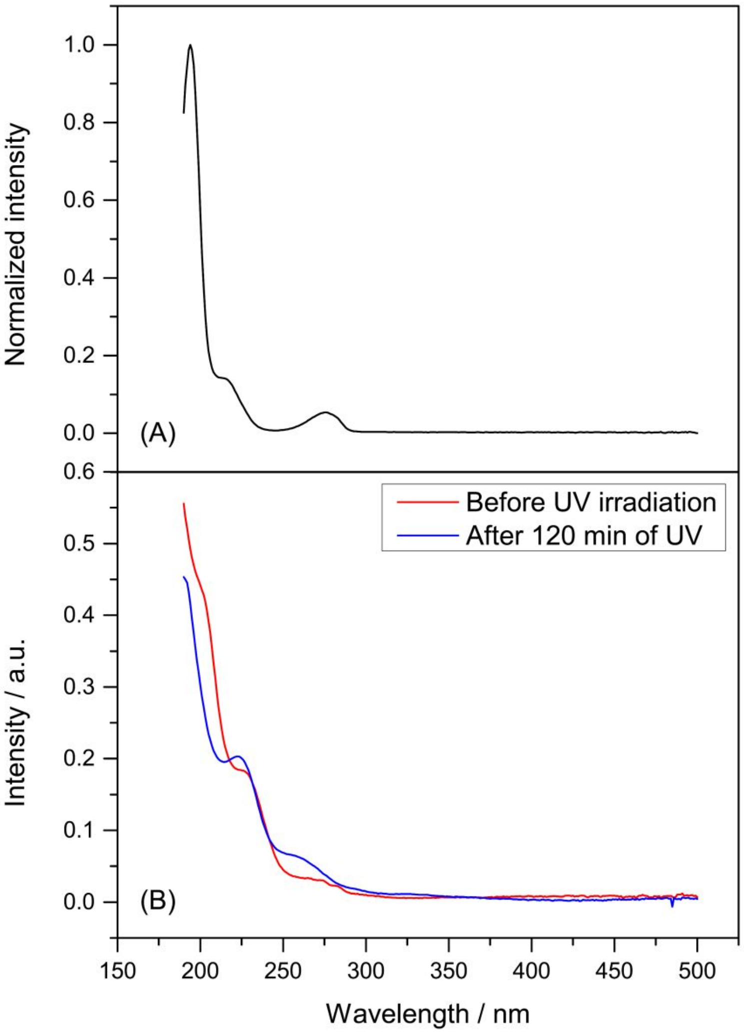

Figure S1. UV spectra of (A) DHB and (B) PAG aqueous solution at pH 7.0. PAG spectra were obtained before and after UV irradiation of 120 minutes.

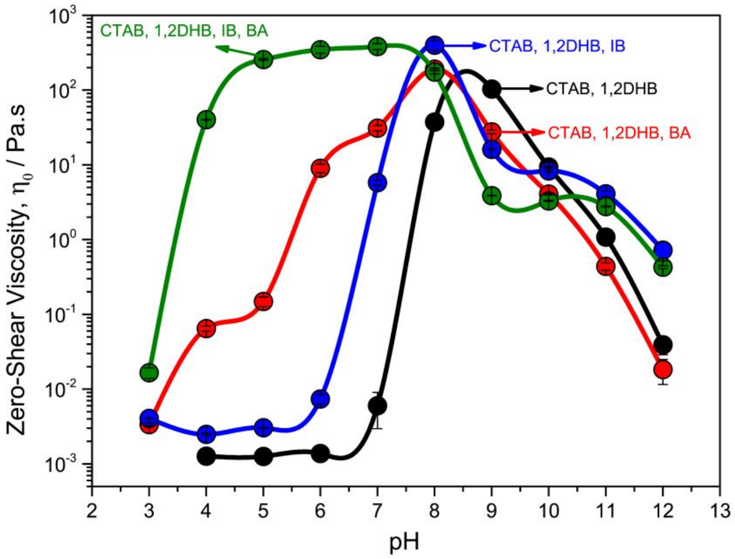

Figure S2. Zero-shear viscosity in Pa s as function of solution pH without irradiation considering the initial and final scenario of irradiation and the influence of each photolysis products in the solution viscosity. The lines are only guide for the eyes. $[CTAB] = [DHB] = 50\ mmol\ L^{-1}$ and $[IB] = [BA] = 10\ mmol\ L^{-1}$ and the average values were obtained from at least a duplicate.

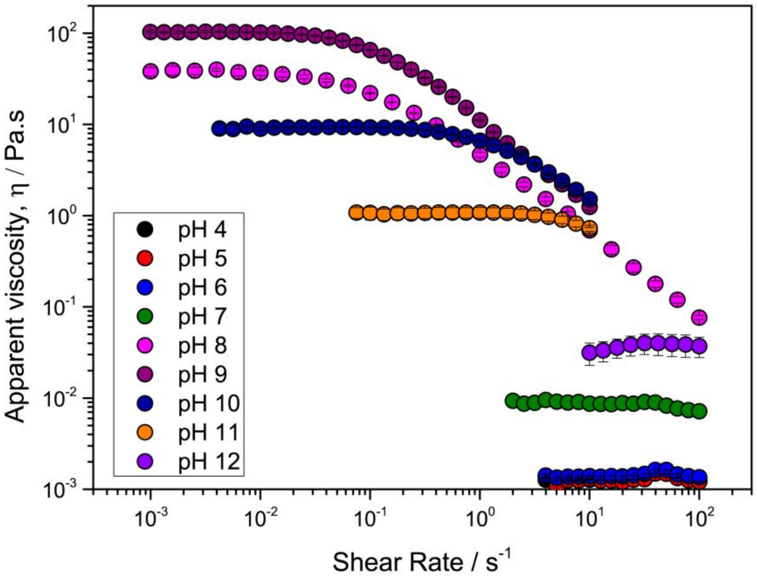

Figure S3. Apparent viscosity as function of shear rate for the solution containing CTAB/DHB in different pH. $[CTAB] = [DHB] = 50.0\ mmol\ L^{-1}$. Values were obtained from at least a duplicate.

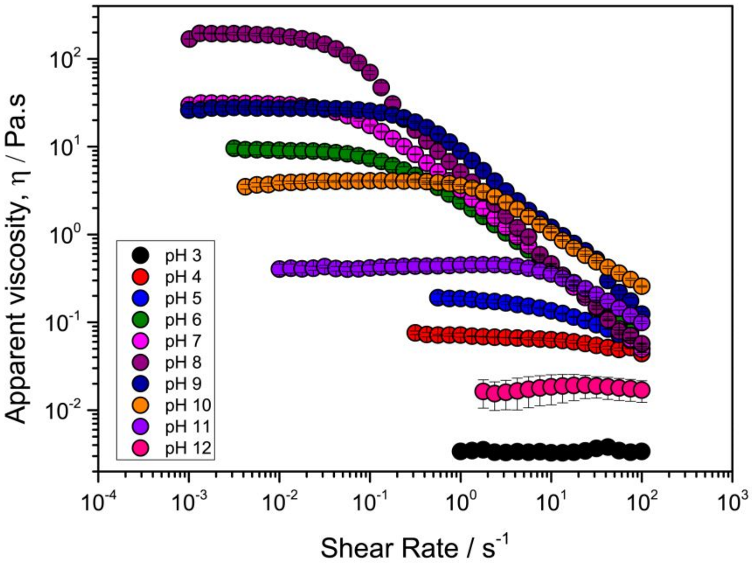

Figure S4. Apparent viscosity as function of shear rate for the solution containing CTAB/DHB/BA in different pH. $[CTAB] = [DHB] = 50.0\ mmol\ L^{-1}$, $[BA] = 10.0\ mmol\ L^{-1}$. Values were obtained from at least a duplicate.

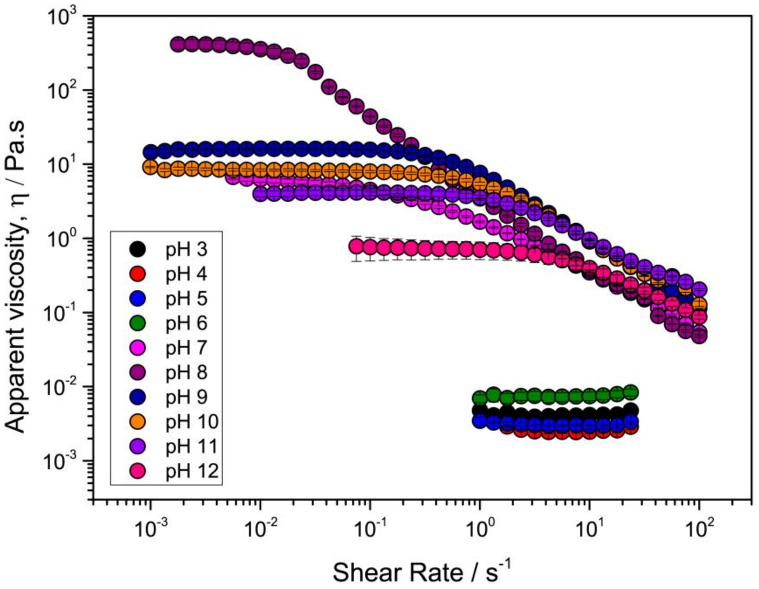

Figure S5. Apparent viscosity as function of shear rate for the solution containing CTAB/DHB/IB in different pH. $[CTAB] = [DHB] = 50.0\ mmol\ L^{-1}$, $[IB] = 10.0\ mmol\ L^{-1}$. Values were obtained from at least a duplicate.

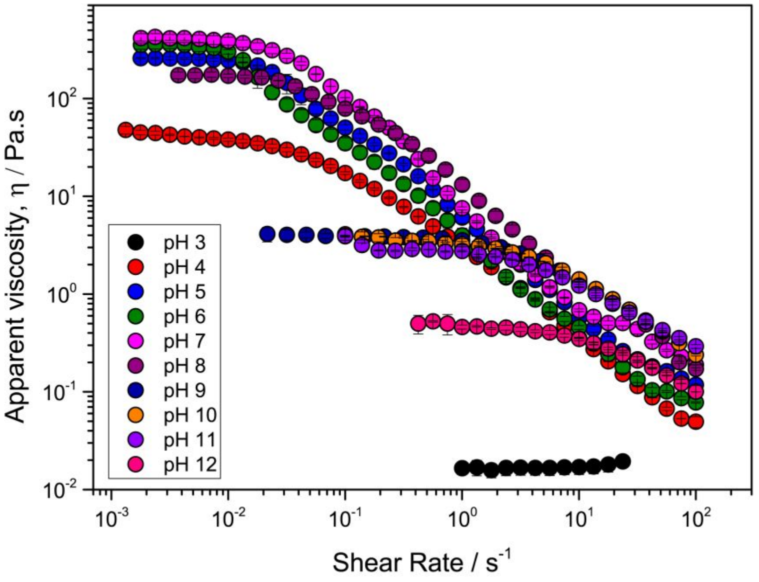

Figure S6. Apparent viscosity as function of shear rate for the solution containing CTAB/DHB/BA/IB in different pH. $[CTAB] = [DHB] = 50.0\, mmol\, L^{-1}$, $[BA] = [IB] = 10.0\, mmol\, L^{-1}$. Values were obtained from at least a duplicate.

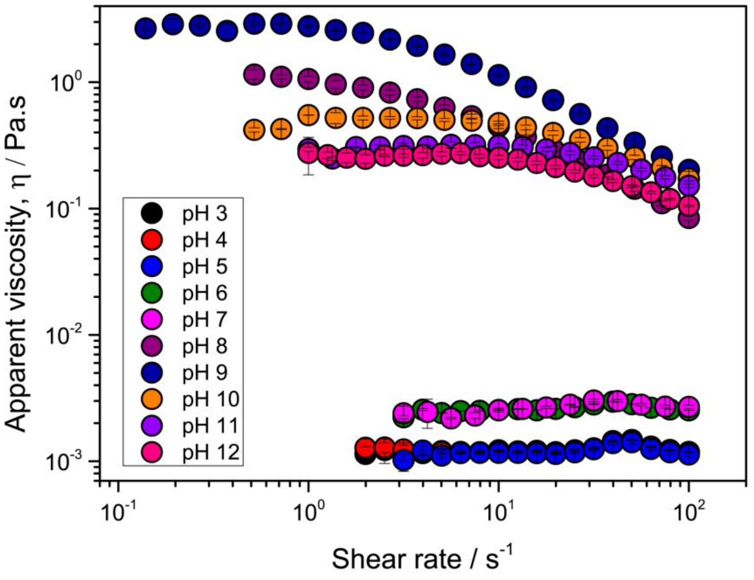

Figure S7. Apparent viscosity as function of shear rate for the solution containing CTAB/DHB/PAG in different pH. $[CTAB] = [DHB] = 50.0\, mmol\, L^{-1}$, $[PAG] = 10.0\, mmol\, L^{-1}$. Values were obtained from at least a duplicate.

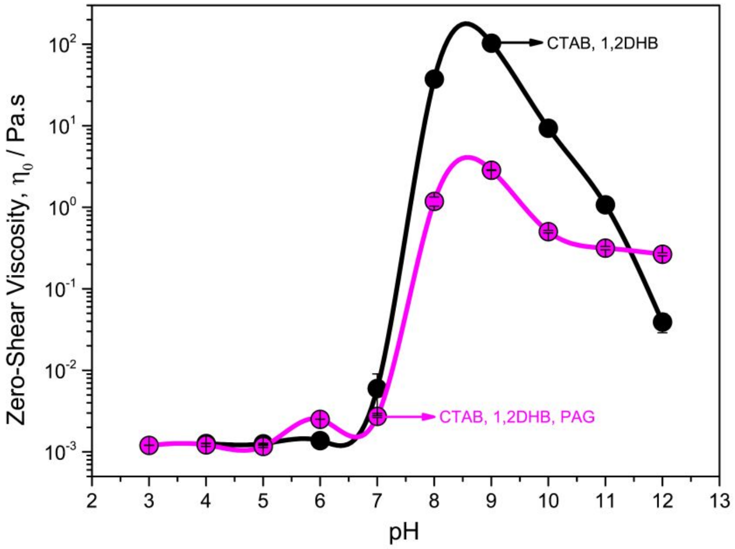

Figure S8. Influence of the PAG in the solution viscosity of CTAB/DHB in different pHs. $[CTAB] = [DHB] = 50\ mmol\ L^{-1}$ and $[PAG] = 10\ mmol\ L^{-1}$. The lines are only guide for the eyes and the values were obtained from at least a duplicate.

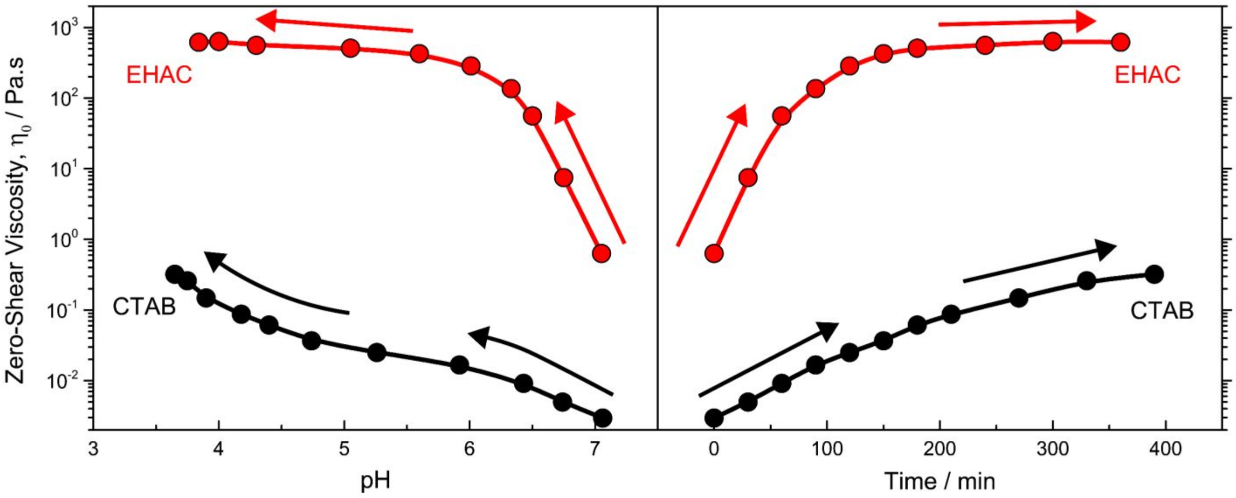

Figure S9. Zero-shear viscosity of the solution containing CTAB or EHAC, DHB and PAG as function of pH and UV irradiation time. $[CTAB] = [EHAC] = [DHB] = 50\ mmol\ L^{-1}$. $[PAG]_o = 10\ mmol\ L^{-1}$ for CTAB solutions and $[PAG]_0 = 15\ mmol\ L^{-1}$ for the EHAC solutions.

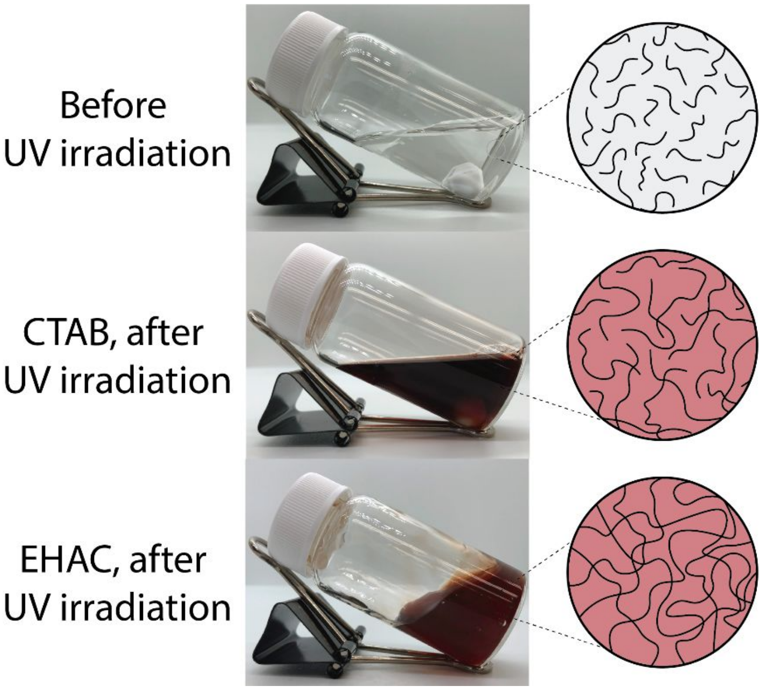

Figure S10. Changes on the solution appearance before and after UV irradiation. The solution contains CTAB or EHAC, DHB and PAG with initial pH 7.0 ± 0.1. $[CTAB] = [EHAC] = [DHB] = 50\ mmol\ L^{-1}$. $[PAG]_o = 10\ mmol\ L^{-1}$ for CTAB and $[PAG]_o = 15\ mmol\ L^{-1}$ for EHAC.

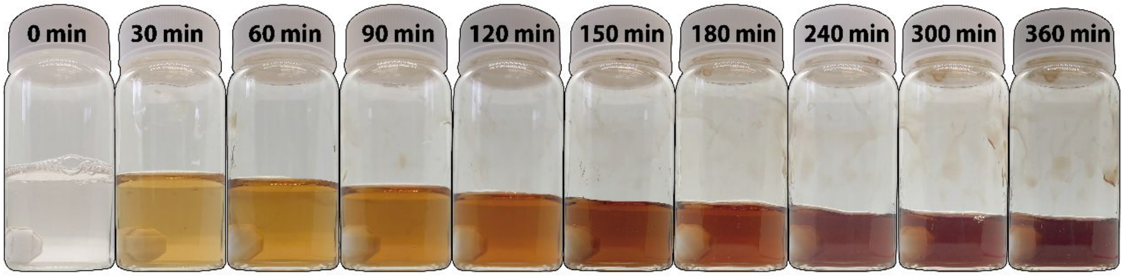

Figure S11. Changes on the solution appearance after shinning UV light with different times. The solution contains EHAC, DHB and PAG with initial pH 7.0 ± 0.1. $[EHAC] = [DHB] = 50\ mmol\ L^{-1}$ and $[PAG]_o = 15\ mmol\ L^{-1}$. The decrease in the volume of the solution occurs by sampling 0.50 mL for the rheological analysis at each UV irradiation time.