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Poly(methyl methacrylate)-Supported Polydiacetylene Films: Unique Chromatic Transitions and Molecular Sensing

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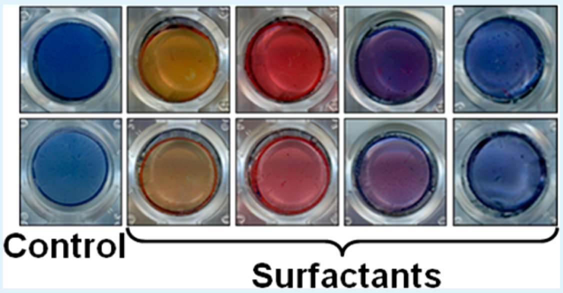
ABSTRACT: Polydiacetylenes (PDAs) constitute a family of conjugated polymers exhibiting unique colorimetric and fluorescence transitions, and have attracted significant interest as chemo- and biosensing materials. We spin-coated PDA films upon poly(methyl methacrylate) (PMMA), and investigated the photophysical properties and sensing applications of the new PDA configuration. Specifically, the as-polymerized blue PDA layer underwent distinct transformations to purple, red, and yellow phases, which could be quantified through conventional color scanning combined with application of image analysis algorithms. Furthermore, we recorded a reversible red-purple PDA transition that was induced by ultraviolet irradiation, a phenomenon that had not been reported previously in PDA film systems. We show that distinct color and fluorescence transitions were induced in the PMMA-supported PDA films by amphiphilic substances—surfactants and ionic liquids—and that the chromatic transformations were correlated to the analyte structures and properties. Overall, this study presents a new chromatic PDA film system in which noncovalent interactions between the PMMA substrate and spin-coated PDA give rise to distinct chromatic properties and molecular sensing capabilities.



KEYWORDS: *polydiacetylene, colorimetric sensors, spin coating, PMMA, thin films*

INTRODUCTION

Polydiacetylenes (PDAs) are π-conjugated polymers displaying unique structural and chromatic properties.[1−8] These polymers, first synthesized in the late 1960s, have attracted considerable interest both scientifically and as promising sensing platforms, primarily because of their visible color transformations (generally from blue to red), induced by varied external stimuli, such as heat,[9] ionic strength,[10] mechanical pressures, and interactions with biological and chemical molecules.[11,12] Modulation of the fluorescence emission of PDA systems which usually accompany the color changes has also contributed to progress in this field as the fluorescence phenomena opened routes for high sensitivity sensing and microscopic imaging.[13,14]

The intriguing chromatic properties of PDA assemblies are believed to arise from the ene-yne topotactic polymerization process, made possible through self-assembly of the diacetylene monomers stabilized through a hydrogen bond network.[15] This generic structural/chromatic feature of PDA systems has been attained in numerous morphologies, including vesicles,[16,17] thin films,[18] fibers,[19] stacked domains,[20] and others. Notably, recent studies have shown that color reversibility (generally from the red phase back to the initial blue phase) could be accomplished through modification of the PDA headgroup moieties.[21] Further expanding the technological and scientific scope of the field has been the demonstration of PDA assemblies exhibiting colors other than blue and red, including yellow and orange PDA.[22−24]

Supported PDA films, in particular, exhibit distinct practical advantages and have attracted considerable interest and research activities.[25,26] Such assemblies are generally robust and stable, and their molecular and macroscopic properties can be better controlled than vesicular systems. Film properties can be also thoroughly analyzed through application of advanced surface characterization techniques.[26] Solid-supported PDA films have been constructed via diverse techniques, including Langmuir monolayers,[27] dip-coating,[28] and spin-coating.[29] Here, we present a study of new PDA films prepared through spin-coating of the diacetylene monomers onto poly(methyl

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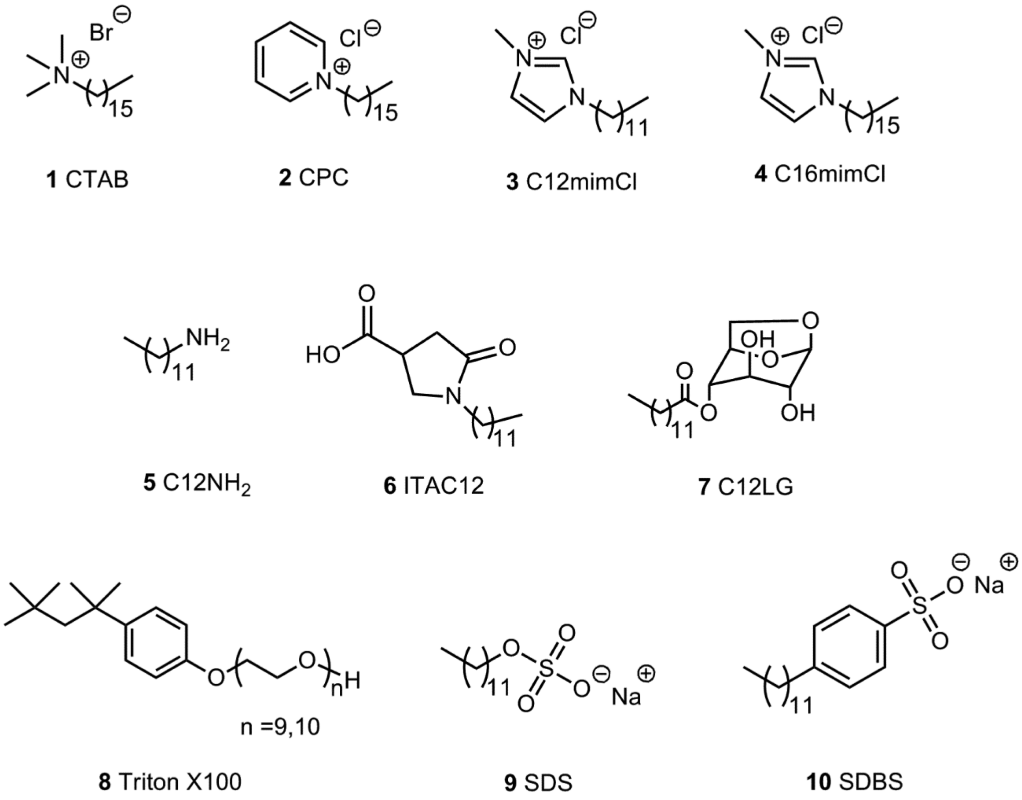
Scheme 1. Structures of the Amphiphilic Compounds Tested: 1, CTAB; 2, CPC; 3, C12mimCl; 4, C16mimCl; 5, C12NH$_2$; 6, ITAC12; 7, C12LG; 8, Triton X-100; 9, SDS; 10, SDBS



methacrylate) (PMMA), a transparent polymer that is widely used in many applications, particularly as a glass substitute.[30] We found that the PMMA substrate intimately affects the deposited PDA films and endows interesting chromatic properties to the system, including chromatic reversibility induced by ultraviolet (UV) irradiation, and purple/red/orange/yellow color transformations affected by interactions with amphiphilic analytes. Specifically, we have tested surfactants classified as cationic, anionic, and nonionic amphiphiles and ionic liquids (ILs) that exhibit surface-active properties because of their structural features.[31]

■ EXPERIMENTAL SECTION

Materials. The diacetylene monomer 10,12-tricosadiynoic acid (TRCDA) and 1-hexadecyltrimethylammonium bromide (CTAB) were purchased from Alfa Aesar; poly(methyl methacrylate) (PMMA, or Perspex) was purchased from Segalovitch Israel; Tetrahydrofuran (THF) and diethyl ether were purchased from Bio-Lab Ltd; Dichloromethane (DCM), ammonium hydroxide, chloroform ($CHCl_3$) and methanol were purchased from Frutarom Ltd; 2,2,2-Trifluoroethanol, Triton X-100, cetylpyridinium chloride (CPC), oxalyl chloride, dodecylamine, 1-chlorohexadecane, 1-chlorododecane, 1-methylimidazole, itaconic acid, 1,6-anhydroglucopyranose (Levoglucosan), lauric acid, *Pseudomonas cepacia* (PS C, lipase immobilized on ceramic particles), acetonitrile, activated charcoal (decolorizing), lithium aluminum hydride ($LiAlH_4$), sodium dodecyl sulfate (SDS), and sodium dodecylbenzenesulfonate (SDBS) were purchased from Sigma-Aldrich. All the reagents and solvents were used as received without further purification.

Synthesis. *10,12-Tricosadiyn Amine.* Synthesis of 10,12-tricosadiyn amine was carried out through a two-step pathway:

(i) TRCDA (570 mg) was dissolved in DCM (20 mL); 2 mL of oxalyl chloride is added two the solution under an argon atmosphere. Several drops of DMF were then added as catalyst. The mixture is stirred at room temperature for overnight. After this, the solvent was evaporated and the residue was dissolved in dry THF (20 mL). The solution was then slowly added to 30 mL of ammonium hydroxide (25 %) in an ice bath and stirred overnight. The solvent was evaporated and the residue was extracted with DCM three times. The organic layer was dried over $MgSO_4$, filtered, and evaporated to dryness.

(ii) The residue obtained in the first step was added to 30 mL of diethyl ether. $LiAlH_4$ (550 mg) was added to it while keeping the solution in an ice bath (***Caution!*** *Do not drop $LiAlH_4$ powder into ice, which causes a violent reaction*). The solution was stirred overnight and then poured into a saturated solution of NH_4Cl. The aqueous layer was then extracted with ethyl acetate. The combined organic layer was washed with saturated NaCl solution and then dried with $MgSO_4$, filtered and evaporated. The residue was purified with column chromatography over silica gel. $CHCl_3$:methanol (9:1) was initially used as solvent, followed by a mixture of 2.5 % NH_4OH in methanol and $CHCl_3$.

Ionic Liquids (ILs). **3**, 1-dodecyl-3-methylimidazolium chloride, C12mimCl; and **4**, 1-hexadecyl-3-methylimidazolium chloride, C16mimCl (the numbers refer to the compounds outlined in Scheme 1, below): ILs **3** and **4** were synthesized according to the procedure reported in the literature[32] by mixing 1-methylimidazole (1 equiv.) with the corresponding chloroalkane (C12 or C16, 1.1 equiv.) at 50 °C. After 24 h, the ILs were washed with diethyl ether (×2) and ethyl acetate (×2) to remove unreacted reagents. After solvent separation the solvent residue was evaporated under reduced pressure. ILs synthesized were dissolved in a small volume of acetonitrile and passed through a thin column of activated charcoal and silica gel to exclude the presence of colored impurities often present in ILs.[33,34]

6:1-lauryl-4-carboxy-2-pyrrolidone, ITAC12 was synthesized under solventless conditions through adapting a published procedure.[35] Briefly, dodecylamine (1 equiv) was added to a two-necked round-bottom flask and heated at 40 °C for few minutes until complete

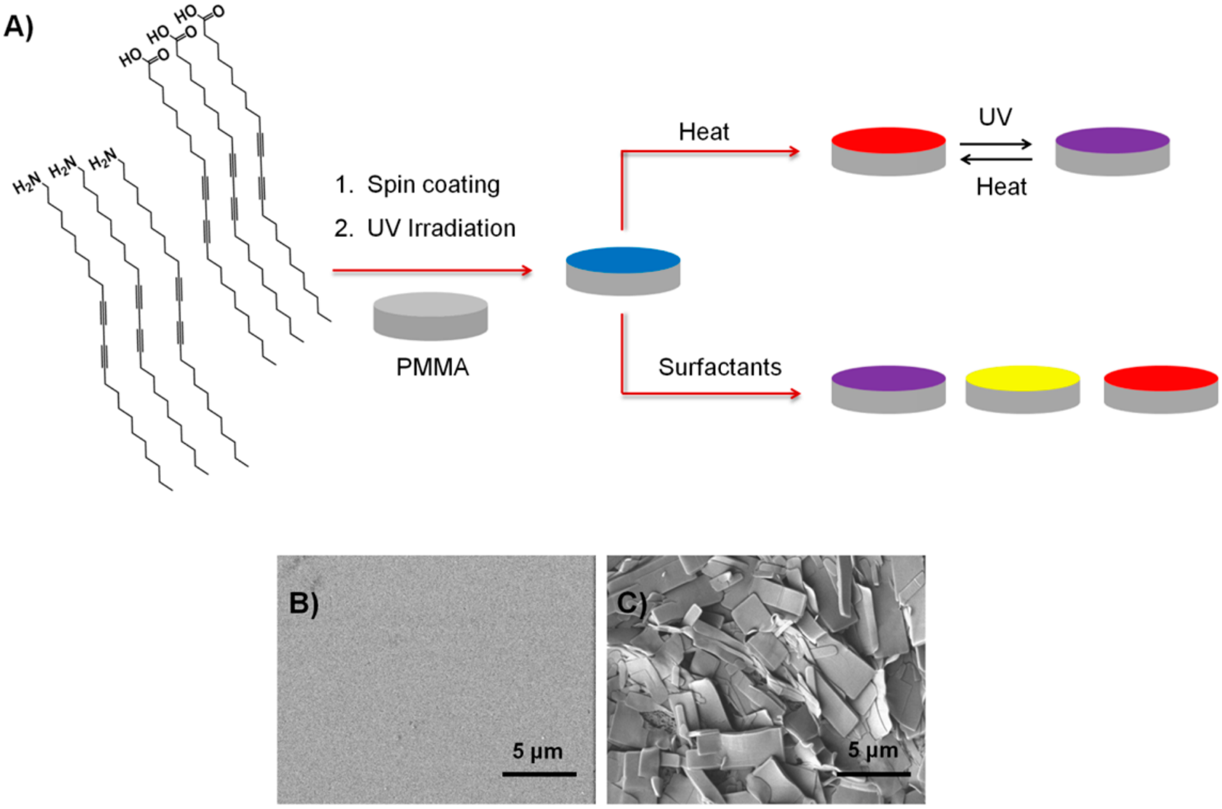


Figure 1. Experimental scheme and film appearance. (A) Experiment summary: monomer solutions (either pure 10,12-tricosadiynoic acid or 10,12-tricosadiynoic acid/10,12-tricosadiyn amine mixture) were spin-coated upon the PMMA substrate and subsequently polymerized by UV irradiation (254 nm). The different color transformations discussed in the text are shown. (B) Scanning electron microscopy (SEM) image of the PMMA substrate used prior to spin-coating. (C) SEM image of the PDA film spin-coated over PMMA.

melting. Itaconic acid (1 equiv) was added to dodecylamine and the mixture heated at 100 °C for 3 h. The reaction was monitored by thin layer chromatography (TLC) (cyclohexane:ethyl acetate = 2:8). The product was purified using column chromatography (cyclohexane/ethyl acetate, gradient elution).

7:4-O-Lauryl-levoglucosan, C12LG was synthesized and purified from levoglucosan and lauric acid by Lipase catalyzed esterification following published procedure.[36]

Film Preparation. The diacetylene monomers (10,12-tricosadiynoic acid and 10,12-tricosadiyn amine) were dissolved in a solvent comprising THF and DCM at a 1:1 ratio in a concentration of 45 mg/mL. The solution was filtered through a membrane filter (Millex, Nylon, 0.45 μm). The PMMA substrates were cut into circular plates of 1 cm diameter. Forty microliters of the monomer was dropped onto the PMMA and after 30 s was spin-coated at 2500 rpm for 30 s using a WS-650 LITE spin coater from Laurell Technologies Corporation, USA.

In the case of the diacetylene mixture, 10,12-tricosadiyn amine was mixed with 10,12-tricosadiynoic acid at a weight ratio of 1:9 and the rest of the procedure was similar to the above procedure for pure 10,12-tricosadiynoic acid. The spin-coated films were irradiated with ultraviolet light (254 nm) for 0.5 min to produce the polymerized, blue phase of polydiacetylene.

Surfactant-Induced Color Change. The tested amphiphilic compounds were first dissolved in the solvent 2,2,2-trifluoroethanol and the solution was diluted to a final concentration of 1 mM by mixing with Trizmabase buffer at pH 8. Polymerized PMMA-coated PDA films were placed in 48-well plates. Three hundred microliters of surfactant solutions (1 mM) was added on top of the PDA−PMMA films and the chromatic changes were recorded.

Quantitative Color Analysis. Quantification of the color transitions was based upon a published procedure for RGB analysis of PDA films.[37] Briefly, 48-well plates containing the spin-coated PMMA-supported PDA films incubated with the amphiphilic compounds were scanned in the transmitted mode on an Epson 4990 Photo scanner to produce 2400 dpi, 24 bit color depth red-green-blue (RGB) images. Digital colorimetric analysis (DCA) was carried out by extracting RGB channel values for each pixel within the sample spots in the scanned images, and the color change values were calculated using Matlab R2010 scientific software (The Mathworks, Inc., MA, USA) as detailed previously.[37] No major changes were made to the program, which allowed us to calculate color change from the blue to yellow phases.

DCA utilizes the standard "red-green-blue" (sRGB) model translating color signals into three distinct values corresponding to the intensities of red (R), green (G), and blue (B) color channels. Accordingly, the relative intensity of a particular RGB component in a scanned image can be defined as the chromaticity level. For example, the yellow chromaticity level (y) in each pixel was calculated as

$$y = (R + G)/(R + G + B)$$

where R (red), G (green), and B (blue) are the three primary color components. For a defined surface area within a PDA-based sensor well we classified a quantitative parameter denoted yellow chromaticity shift (YCS) that represents the blue-red and blue-red-yellow transformations of the pixels in the analyzed film area

$$\mathrm{YCS} = (y_{\mathrm{sample}} - y_0)/(y_{\max} - y_0)100\%$$

where y_{sample} is the average yellow chromaticity level of all pixels in the scanned surface, y_0 is the average yellow level calculated in a blank surface (blue PDA film) and $y_{\max}$ is the average yellow chromaticity level of the maximal blue-yellow transition occurring at the PDA film. In essence, YCS is the normalized change in the chromaticity level within the sensor well surface on which the tested sample was deposited.

UV−Vis Spectroscopy. UV−vis spectroscopy measurements were carried out at 23 °C on a Varioskan (Thermo, Finland).

Fluorescence Spectroscopy. Forty-eight-well plates containing the PMMA-coated PDA films were placed in a multiwall fluorescence plate reader (Varioskan, Thermo, Finland) at 23 °C. All measurements were carried out using 482 nm excitation. The curves obtained were smoothed by using a 10 point adjacent averaging.

Raman Scattering. Raman spectra were recorded with a Jobin-Yvon LabRam HR 800 micri-Raman system, equipped with a liquid-N_2-cooled detector. The excitation source was an Argon laser (514 nm), with a power of 5 mW on the sample. In order to protect the samples the laser power was reduced by 1000 using ND filters. The laser was focused with 100× long-focal-length objective to a spot of about 4 μm. Measurements were taken with the 600 g mm^{-1} grating and a confocal microscope with a 100 μm hole with a typical exposure time of 1 min.

Scanning Electron Microscopy (SEM). Scanning electron microscopy (SEM) images were recorded on a JEOL JSM-7400F (Tokyo, Japan) Scanning Electron Microscope. Images were taken after sputtering a thin film of Au (~15 nm thickness) over the substrates for better contrast and minimum charging.

RESULTS AND DISCUSSION

Figure 1 depicts the experimental scheme and the film morphology. Two diacetylene monomers were employed: 10,12-tricosadiynoic acid displaying a carboxylic moiety, and 10,12-tricosadiyn amine in which the carboxylic residue was substituted with an amine. The monomers, dissolved in a THF/DCM mixture (1:1), were deposited through spin-coating upon circular-shaped PMMA substrates. Following drying and ultraviolet irradiation (254 nm), the PDA/PMMA films (produced by using only 10,12-tricosadiynoic acid), as well as PDA-NH_2/PDA/PMMA (produced by using 1:9 mol ratio mixture of 10,12-tricosadiyn amine and 10,12-tricosadiynoic acid) turned intense blue due to the conjugated π-system of the planar polydiacetylene network.[1] As outlined in Figure 1A, the blue PDA/PMMA films underwent further colorimetric transformations into purple, red, or yellow, induced by external stimuli, discussed in detail below. Images B and C in Figure 1 present SEM images of the PMMA surface before and after spin coating, respectively. The initial PMMA surface was flat and uniform (Figure 1B). Spin-coating of PMMA with diacetylene and subsequent polymerization resulted in appearance of irregularly-shaped rectangular PDA domains previously detected in varied film and vesicle configurations[38] (Figure 1C).

Figure 2 highlights the colorimetric transformations of PMMA-supported PDA films induced by heating and subsequent UV irradiation (similar results were recorded in case of spin coating of the PDA-NH_2/PDA mixture, data not shown). Following heating (5 min at 80 °C), the PDA/PMMA films underwent the well-known blue-red transformation[9] (Figure 2A). Intriguingly, however, the red film became gradually purple upon subsequent irradiation with UV light (254 nm for 30 s, Figure 2A). It should be noted that longer irradiation times of the red PDA/PMMA films did not produce a complete back-transformation to blue color. Furthermore, the red-purple transformation was not affected by the extent of initial irradiation time−similar colorimetric results were recorded even when significantly longer initial irradiation was carried out (up to 10 min), making sure that complete PDA polymerization was achieved.

Spectroscopic analyses in Figure 2B-D indicate that the purple appearance corresponds to a back-transformation of the PDA film into a blue polymer phase. The UV-vis spectra in Figure 2B confirm that UV irradiation resulted in re-emergence of the peak at around 650 nm corresponding to the blue PDA phase. Similarly, the fluorescence emission data in Figure 2C reveal a dramatic attenuation of the PDA fluorescence of the red sample following uv irradiation, corroborating the hypothesis that the UV-induced purple phase of the PDA/PMMA film corresponds to a unique red-blue transformation of PDA. The Raman scattering data in Figure 2D lend support to this interpretation, clearly showing that UV irradiation of the red PDA/PMMA films resulted in re-emergence of the prominent peaks at 1450 and 2090 cm^{-1} associated with the blue PDA phase.[39] Importantly, the red-purple transition was reversible, and the red phase of the film re-appeared after heating. It should be noted that while several studies had reported temperature-cycled reversible blue-red transformations of PDA systems,[40,41] the UV-induced reversible red-blue transition highlighted in Figure 2 has not been previously reported in the literature for PDA films. This phenomenon is even more remarkable in light of the well-known effect of UV irradiation as an accelerant of blue-red transitions in PDA vesicles and films.[39]

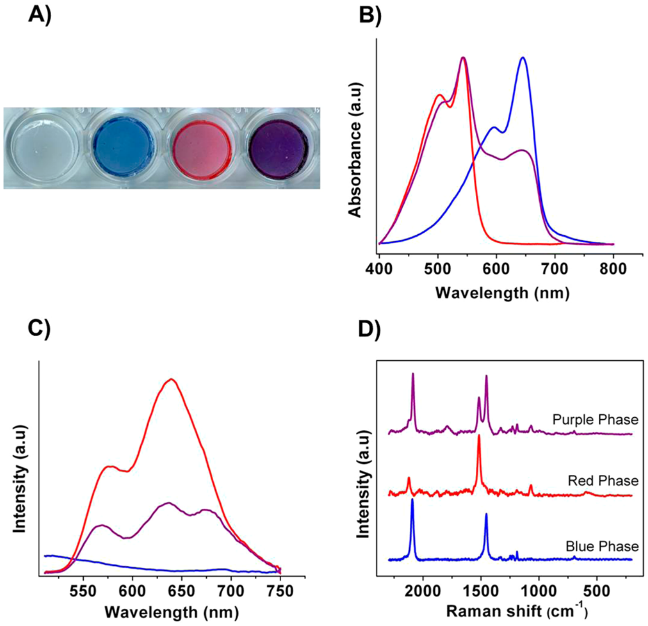


Figure 2. Chromatic transformations induced by heat and ultraviolet irradiation. (A) Scanned images of PMMA-supported PDA films undergoing heat-induced blue-red transition and subsequent red-purple transformation induced by UV irradiation; (B) UV−vis absorption spectra of the PMMA-supported PDA films shown in A; (C) fluorescence emission spectra of the PMMA-supported PDA films shown in A; (D) Raman spectra of the PMMA-supported PDA films shown in A.

The chromatic transformations of PDA systems have been widely exploited towards development of biological and chemical sensing applications.[12,42,43] Accordingly, we investigated the chromatic response of the new PMMA-supported PDA films upon addition of different analytes (Figures 3−5). The PDA/PMMA film assemblies are particularly attractive as a sensing platform since they are physically robust and stable, exhibit color durability for long time periods (months) and are amenable for mass production. Scheme 1 presents the structures of representative amphiphilic molecules tested in this study. Specifically, we examined amphiphilic compounds (compounds **1**−**10**, Scheme 1) belonging to different classes,

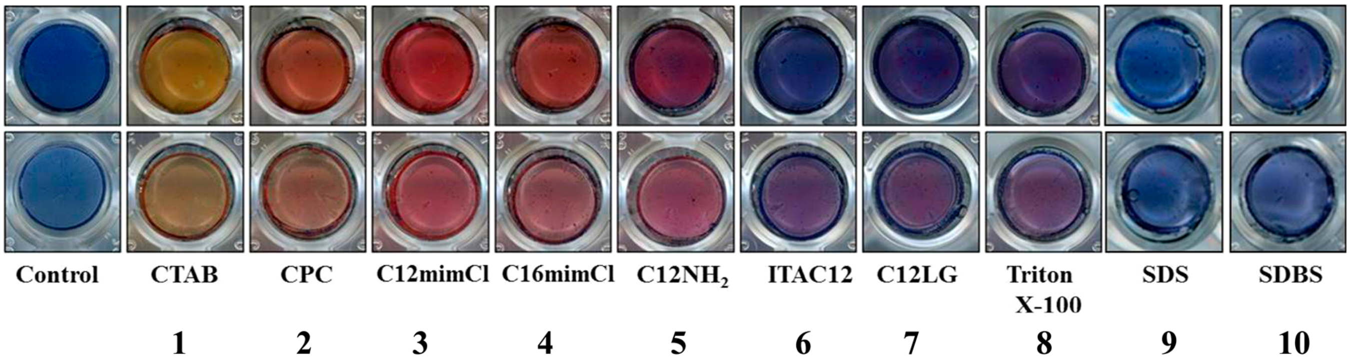


Figure 3. Color transitions induced by the amphiphilic analytes. Scanned images of PDA/PMMA (top row), and PDA-NH$_2$/PDA/PMMA (bottom row), after addition of the surfactants (concentrations 1 mM). Images were recorded after 40 min incubation.

including cationic surfactants [1-hexadecyltrimethylammonium bromide (CTAB) **1**, and cetylpyridinium chloride (CPC) **2**], ionic liquids (ILs) [1-dodecyl-3-methylimidazolium chloride (C12mimCl) **3**, and 1-hexadecyl-3-methylimidazolium chloride (C16mimCl) **4**], weak acid/base surfactants [dodecylamine, **5**, 1-lauryl-4-carboxy-2-pyrrolidone (ITAC12) **6**], *non-ionic* surfactants [4-O-lauryl-1,6-anhydroglucopyranose (C12LG) **7**, and Triton X-100 **8**], and anionic surfactants [sodium dodecyl sulfate (SDS) **9** and sodium dodecylbenzenesulfonate (SDBS) **10**].

Our choice of analytes was aimed to test a broad range of reagents and environmentally-sensitive solutes exhibiting different structures, charge, and functional units. Specifically, we examined nitrogen-, oxygen-, and sulphur- containing molecules having the same chain lengths (12 carbon atoms for compounds **3**, **5**, **6**, **7**, **9** and **10** and 16 carbon atoms for compounds **1**, **2**, and **4**) but displaying different charges (or no charges) in the polar head. Compounds **5**, **6**, and **7** can be considered as representative renewable surfactants, synthesized from renewable resources.[44] Specifically, primary amines such as compound **5** are produced in industrial processes from lauric acid;[45] **6** is obtained from the reaction of itaconic acid and dodecylamine **5**. Itaconic acid is industrially obtained with high yields in biotechnical processes using substrates like sucrose, glucose, starch hydrolysates, or purified molasses and fungi of the genus *Aspergillus*.[46] **7** is obtained through enzyme acylation of levoglucosan, a common anhydro-sugar, produced in high yields from the pyrolytic treatment of cellulose.[47]

Figure 3 presents scanned images of the color transformations induced by the analytes upon incubation with PDA/PMMA and PDA-NH$_2$/PDA/PMMA. The choice of the two specific sensor compositions was aimed at assessing the effect of varying the PDA headgroup upon the chromatic properties and transformations. The images in Figure 3 clearly show that the surfactants induced distinct color changes upon incubation with the films. Furthermore, differences in color transitions are also apparent between films containing the two PDA derivatives.

Specifically, CTAB (**1**) induced a striking blue-yellow transformation upon incubation with the PDA/PMMA film, and yellow-orange color in the case of PDA-NH$_2$/PDA/PMMA. In comparison, CPC (**2**) and the ILs displaying positively *charged* bulky headgroups **3** and **4** gave rise to orange-red colors when added to PDA/PMMA, and orange-purple shades upon addition to PDA-NH$_2$/PDA/PMMA. It appears that the difference in the length of the alkyl chains of ILs **3** and **4** (four carbon atoms) did not play a role in inducing color changes. Although the ionic compounds **1**−**4** and the amine **5**, which also is partially protonated in the experimental conditions, induced significant color changes, as shown in Figure 3, the carboxylate-type surfactant **6**, the nonionic surfactants **7** and **8**, and anionic surfactants **9** and **10** produced small or insignificant color changes in the PDA/PMMA system and blue-purple transitions upon incubation with the PDA-NH$_2$/PDA/PMMA films (in case of the nonionic surfactants, Figure 3).

The color changes of the PDA/PMMA films can be quantified through application of a simple image analysis algorithm,[37] providing the means for both comparing the different colors induced, as well as evaluating the time-dependent colorimetric transformations (Figure 4). The kinetic curves in Figure 4 represent the extent of color transformations through combining image analysis of scanned images such as shown in Figure 3 with summation of the red-blue-green components in each pixel.[37] Essentially, the %RGB scale

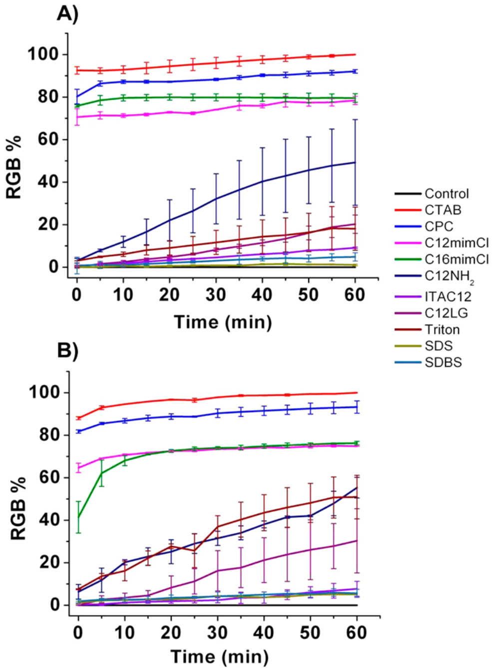


Figure 4. Quantitative kinetic color curves. Time-dependent %RGB curves reflecting the extent of blue-red-yellow transformation of the (A) PDA/PMMA film and (B) PDA-NH$_2$/PDA/PMMA film after addition of compounds **1**−**10**.

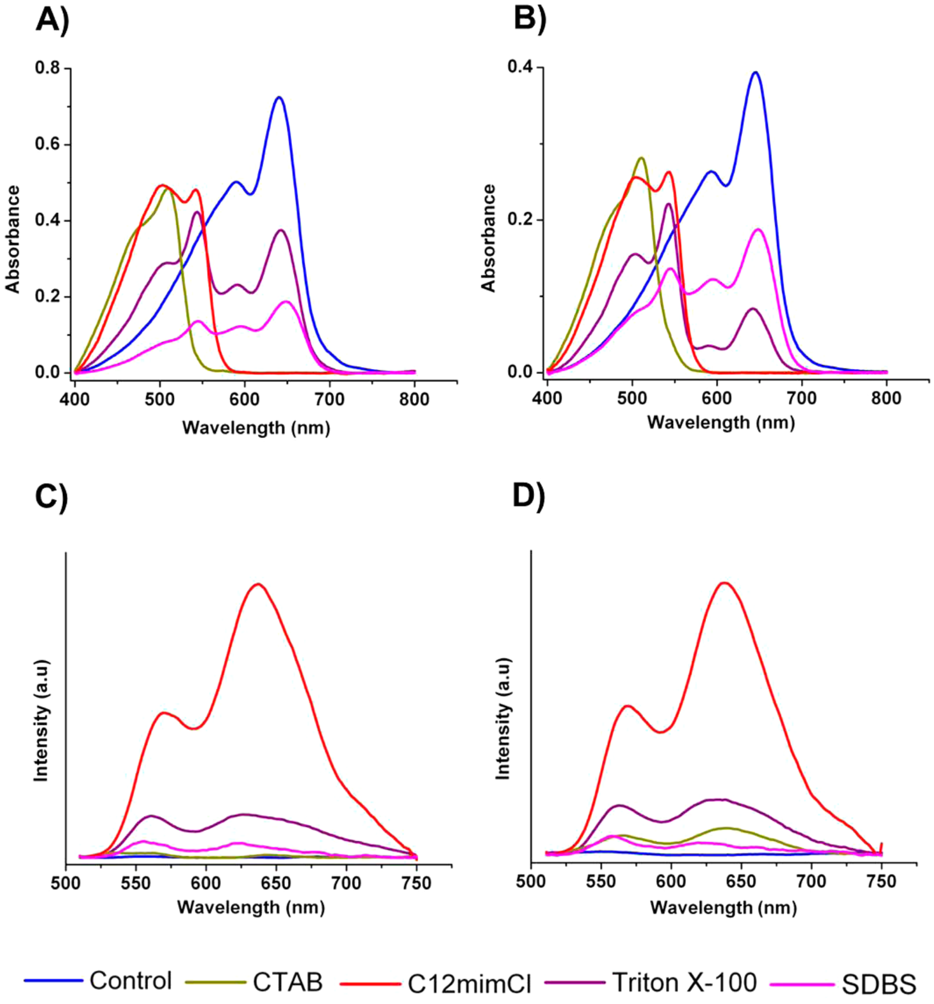


Figure 5. Spectroscopic characterization of PMMA-supported PDA films undergoing distinct color transitions. The four compounds shown represent different color transitions: CTAB (yellow); C12mimCl (red); triton X-100 (purple); SDBS (magenta). (A) UV−vis absorbance spectra of PDA/PMMA; (B) UV−vis absorbance spectra of PDA-NH_2/PDA/PMMA; (C) fluorescence emission spectra of PDA/PMMA, excitation 482 nm; (D) fluorescence emission spectra of PDA-NH_2/PDA/PMMA, excitation 482 nm.

measures the blue-red-yellow transformations, in which high values correspond to the appearance of a yellow color, whereas lower %RGB reflects less pronounced color transitions (e.g., blue-purple and blue-red).

The %RGB analysis in Figure 4 underscores the significantly different color transformations both recorded among the compounds tested, and also between the two PDA film compositions. Specifically, high %RGB values were recorded when the cationic surfactants (**1** and **2**) or ILs (**3** and **4**) were added. These compounds furthermore induced almost instantaneous colorimetric transformations (Figure 4). The nonionic surfactants (**7** and **8**), on the other hand, gave rise to much lower %RGB values which gradually increased over time. This result likely reflects slow adsorption of these surfactants onto the PDA films. Note, however, that the %RGB graphs in Figure 4 clearly show that the non-ionic surfactants gave rise to greater color transformations upon addition to the PDA-NH_2/PDA/PMMA films, reflecting the enhanced adsorption to the polar amine moieties. Figure 4 also demonstrates that the anionic surfactants **9** and **10** induced negligible color changes that are ascribed to electrostatic repulsion to the PDA units that exhibit residual negative charge. A similar result was recorded in case of **6**, which is anionic at the pH condition employed in the experiments (pH 8).

Interestingly, the %RGB curve recorded for dodecylamine (**5**) appears different than the other surfactants tested, initially inducing low %RGB values while rapidly increasing after a few minutes. This distinct kinetic behavior is probably related to the much smaller headgroup of **5** as compared to the other surfactants examined, and/or to the presence of the basic nitrogen. Importantly, the quantitative kinetic analysis in Figure 4 underscores the differences between the chromatic responses of PDA/PMMA and PDA-NH_2/PMMA: the ionic compounds induced higher %RGB when incubated with the (negatively-charged) carboxyl-displaying film, whereas the nonionic surfactants generally gave rise to steeper %RGB kinetic curves in case of PDA-NH_2/PDA/PMMA.

To shed light upon the colorimetric transitions induced by the surfactants in the PDA/PMMA films we carried out spectroscopic analyses (Figure 5). Specifically, we recorded UV−vis spectra and fluorescence emission of representative films, together providing insight into the photophysical properties of the distinct PDA phases formed. The UV−vis spectra in panels A and B in Figure 5 reveal that the yellow PDA phase (induced by incubation of the PDA/PMMA or

PDA-NH_2/PDA/PMMA films with CTAB) exhibits a distinct absorbance peak at ~500 nm.[24] The red-orange PDA phase (shown is the UV−vis absorbance of the PDA/PMMA or PDA-NH_2/PDA/PMMA following incubation with C12mimCl), however, displays the typical absorbance of red-phase PDA at around 540 nm,[23] although the shoulder apparent in a lower wavelength suggests a contribution from the yellow PDA phase. The purple PDA/PMMA (induced by Triton X-100) gave rise to UV−vis spectra that either reflect incomplete blue-red transformation, or a mixture of the blue and red phases.[48]

Dramatic differences between the analyte-induced chromatic transformations are apparent in the fluorescence *emission* spectra (excitation 482 nm, Figure 5C, D). Surprisingly, the fluorescence spectra show that the yellow PDA film (following addition of CTAB) hardly exhibits fluorescence emission, similar to the nonfluorescent blue PDA. This observation, not reported previously, echoes the shifted visible absorbance peak recorded for the yellow PDA/PMMA films (Figure 5A-B) and indicates that the yellow phase corresponds to a distinct PDA organization. In a sharp contrast, the red-phase PDA, formed through incubation of PDA/PMMA or PDA-NH_2/PDA/PMMA with C12mimCl, was highly fluorescent (red curves in Figure 5C, D), whereas the purple PDA/PMMA films (induced by Triton X-100) produced intermediate emission spectra. Together, the UV−vis and fluorescence emission data in Figure 5 indicate that the dramatic color transitions recorded, i.e., blue-purple, blue-red, and blue-yellow (Figures 3 and 4), are associated with formation of distinct PDA phases. Moreover, the spectroscopic data in Figure 5 corroborate the colorimetric analysis above, and confirm that binding of molecules from each analyte family resulted in different structural/photophysical PDA transformations.

■ CONCLUSIONS

In conclusion, we present a new PDA film assembly deposited via noncovalent interactions (i.e., spin-coating) upon transparent PMMA substrates. The PDA/PMMA systems exhibit interesting chromatic properties, likely related to the specific molecular rearrangement at the PDA/PMMA interface. Indeed, the solvent mixture employed for spin-coating the diacetylene monomers upon the PMMA substrate (THF/DCM) induces partial dissolution of the polymer surface area, thereby enabling more pronounced internalization of the pendant PDA side-chains within the polymer network. Specifically, we observed a unique red-purple transformation induced upon uv irradiation—reflecting a reversible transition from the red PDA phase back to the initial blue phase. Furthermore, we detected distinctive colorimetric and spectroscopic transformations, corresponding to purple, red, and yellow PDA phases specifically induced by different surfactant classes. Overall, this work introduces a new polymer-supported PDA film construct exhibiting interesting structural, photophysical, and sensing properties.

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Notes

The authors declare no competing financial interest.

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