Retarded evaporation-induced synthesis of lamellar block copolymer supramolecules for solvatochromic sensing

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ABSTRACT

The responses of conventional solvatochromic sensors to stimuli are usually performed by generating changes in absorption and emission bands based on the polarity of solvents. However, there still remains a high risk of the overlapped bands for the solvents with similar polarities, resulting in a tough realization of the visual colorimetric differentiation. Here, we develop an innovative solvatochromic sensor in the form of film self-assembly of block copolymer supramolecules. The produced sensor consists of alternating layers of two phases, in which one is polystyrene (PS) and the other is the combination of poly (4-vinylpyridine) (P4VP) and polydiacetylene (PDA). Owing to the fact that PDA is embedded into P4VP, the inherent protection of PDA by block copolymers is thus guaranteed in such lamellar structures. The specific organic solvents with a strong affinity to PS could merely penetrate into the supramolecular lamellae followed by interacting with thus-exposed PDA, leading to the realization of solvatochromism. By incorporating the heating-induced blue-to-red color transition (thermochromism) with solvatochromism of the sensor, a straightforward technique to realize the nonvisualization of an imprint followed by its revisualization is developed.

1. Introduction

The recognition of organic solvents is a challenging task in chemistry [1]. To this end, selective solvatochromic sensors have been widely developed based on various materials, for instance, gels [2], silicon elastomers [3], organic small molecules [4–7], MoS₂ monolayers [8] and metal-organic frameworks [9], etc. The conventional solvatochromic sensors are commonly dependent on the shift of the emission sequence, however, will be largely interfered by the band overlap when the organic solvents with similar polarities are differentiated. Therefore, the visual differentiation of the solvents is, to some extent, limited for solvatochromism.

PDA, a conjugated polymer with extremely intriguing optical properties on account of the extensively delocalized π-electron backbones, has been broadly used for preparing chemo-sensors [10–14]. Owing to the facile preparation by UV or γ irradiation-induced polymerization of diacetylene (DA) monomers, PDA has been an ideal candidate to realize the blue-to-red color transition in response to environmental perturbations such as organic solvents (solvatochromism) and heat (thermochromism), etc [15]. Therefore, a wide variety of chemo-sensors based on PDA have been fabricated to meet the needs of solvatochromism so far [16–18]. Unfortunately, poor-quality PDA films are usually prepared by directly drop- or spin-coating DA monomers on substrates due to the strong aggregation of the monomers [15]. To tackle this issue, DA-embedded matrix materials were then proposed as an alternative avenue to prepare PDA chemo-sensors, for instance, microfibers [16,19,20] and monolithic films [21,22]. These supramolecular structures, constructed by the hydrogen bonds based on DA and matrix materials, have been regarded as ideal candidates to produce the desired sensors [23–28]. And the sensors have displayed excellent solvatochromic properties and could distinguish organic solvents efficiently [16,29]. However, the visual differentiation imposed by the indiscriminant response of PDA to organic solvents is still difficult to be realized. To solve this problem, protective layers have thus been designed to be coated onto PDA films [1]. In this case, due to the protective layer-induced selective contact of PDA to organic solvents, solvatochromism can be enhanced. But time-consuming and tedious procedures are generally required to seek and build compliant protective layers for distinguishing organic solvents.

Block copolymers (BCPs) are well-known polymeric materials and capable of self-assembling into abundant morphologies, which could...
provide DA a lot of promising matrices [30]. Moreover, a wealth of small molecules with hydroxyl or carboxyl groups have been demonstrated to be hydrogen bonded to the free pyridine groups of the BCP of polystyrene-block-poly(4-vinylpyridine) (PS-b-P4VP) [31–34]. Therefore, DA monomers with the carboxyl groups possess the ability to be complexed with PS-b-P4VP [23]. The resultant phase-separated morphologies with well-defined structures can be observed in our previous work [35]. The BCP matrix in which DA embed could serve as the inherently protective layers, leading to the selective contact of DA-derived PDA to organic solvents. Then solvatochromism is available for the recognition of the specific solvents. It is also worth noting that though various framework materials have been employed to produce PDA colorimetric sensors, BCPs are rarely used to be the polymeric matrices embedded with PDA.

In this work, the amphiphilic block copolymer of PS-b-P4VP is hydrogen-bonded to PDA monomers (10, 12-pentacosadiynoic acid, donated as PCDA) to self-assemble into supramolecular lamellae with alternating PS and P4VP(PCDA) layers. With UV irradiation, PCDA are further photopolymerized as blue PDA, yielding P4VP(PDA) instead of P4VP(PCDA) in supramolecular lamellae. Meanwhile, the cross-linking of PS-b-P4VP is acquired. Attributing to the intrinsic protection of PDA by the cross-linked BCP lamellae, the produced supramolecular films exhibit a high selectivity for the contact of PDA to the specific organic solvents. This well-designed sensor provides an accessible avenue to realize the recognition of specific organic solvents via the colorimetric transition. Moreover, the produced supramolecular film also exhibits a blue-to-red color transition upon heating, which is further incorporated with solvatochromism to realize the nonvisualization of an imprint followed by its revisualization.

2. Experimental

2.1. Materials

Block copolymer of PS-b-P4VP (Mₐ,PS = 75 kg/mol, Mₐ,P4VP = 25 kg/mol, and the polydispersity = 1.09) was purchased from Polymer Source, Inc. (Canada), and used as received. 10, 12-pentacosadiynoic acid (PCDA) was purchased from Alfa Aesar with purity higher than 98%. Before use PCDA was dissolved in chloroform and filtered twice to remove the pre-polymerized parts by polytetrafluoroethylene (PTFE) filters with a nominal average pore size of 0.22 μm. Chloroform (CHCl₃, purity ≥ 99.9%), tetrahydrofuran (THF, purity ≥ 99.9%), dichloromethane (CH₂Cl₂, purity ≥ 99.8%), acetone (purity ≥ 99.9%), ethanol (purity ≥ 99.5%), ethyl acetate (EA, purity = 99.8%), toluene (purity = 99.8%), isopropanol (IPA, purity = 99.5%) and hexane (purity ≥ 97%) were obtained from Sigma Aldrich and used without further purification. Glass substrates with a size of 4 cm × 4 cm were ultrasonicated at least three times in ethanol followed by air-drying before use.

2.2. Preparation of supramolecular films with lamellar structures

PS-b-P4VP was dissolved in chloroform to produce solutions with a concentration of 0.5 wt%. PCDA was then added into such BCP solutions to increase the concentration of PS-b-P4VP(PCDA) to 0.75 wt%. In such case, the mass fraction of P4VP(PCDA) can be estimated as ca. 50%, which is in favour of preparing supramolecular lamellae according to our previous work [35]. Meanwhile, the molar ratio of PCDA/4VP was calculated as ~0.56. The solutions were stirred at room temperature for at least 12 h for the complete generation of hydrogen bonds between PCDA and 4VP. Before use the supramolecular solutions were filtered three times through PTFE filters with a nominal average pore size of 0.22 μm to remove any big aggregates. To prepare the aligned supramolecular film with lamellar structures, 600 μL supramolecular solutions were drop-cast onto a glass substrate, which were then covered instantly by a petri dish to control the duration of solvent evaporation as ca. 2 h at room temperature (ca. 18 °C). Finally, a transparent supramolecular film with a thickness of ca. 6 μm was yielded on the glass slide after the complete evaporation of chloroform [35].

2.3. Recognition of organic solvents and characteristics

The supramolecular film surface was analyzed by a contact angle goniometer (DropMeter A100, Maist). The supramolecular films were subjected to UV irradiation (λ, = 254 nm) with 1 mW/cm² for different durations to acquire the visual transparency-blue transition. To distinguish organic solvents by the supramolecular film, 5 μL organic solvents were dropped onto the UV-irradiated film surface and held for 30 s. Afterwards, a digital photo was taken by a camera (G10, Canon) regardless of whether or not the complete evaporation of solvents. To realize the nonvisualization of an imprint followed by its revisualization in the supramolecular film, 50 μL isopropanol were used as “ink” to “write” the imprint on the 3 min UV-irradiated film surface at first. Such film was further thermal-treated at 100 °C for 3 min followed by UV irradiation with 3 min. The visible spectra of the films were collected at a UV–vis-NIR spectrophotometer (UV-3600, Shimadzu) with the wavelength ranging from 400 nm to 800 nm. The optical images were taken using an Olympus MVX10 stereomicroscope with color CCD camera. The excitation wavelength was set at 395 nm. Fluorescent images were recorded on the Leica TCS/SP2 confocal microscope system with the excitation wavelength of 488 nm.

Field-emission scanning electron microscopy (Hitachi, S4800) was used to observe surfaces and cross sections of the films at a voltage of 5 kV. Before SEM examinations the samples were sputter-coated with a thin layer of Pd/Pt alloy. Fourier transform infrared spectroscopy (FTIR) spectra were obtained from a Nicolet 8700 infrared spectrometer in the attenuated total reflection (ATR) mode. Small-angle X-ray scattering (λ, = 0.124 nm) was used to investigate the structure of the supramolecular film with a thickness of 6 μm. The voltage was 10 kV. Moreover, the duration of X-ray exposure was designated as 400 s. Sample-to-detector distance is 1.94 m. The scattering vector q is defined as q = (4π/λ) sin θ, and 2θ is the scattering angle.

3. Results and discussion

3.1. Sensing course

The free pyridine of PS-b-P4VP can be easily hydrogen-bonded to the hydroxyl or carboxyl groups of small molecules, capable of producing the supramolecules comprised of PS-b-P4VP and small molecules [35–37]. Hence, 10, 12-pentacosadiynoic acid (PCDA) is able to be hydrogen-bonded to PS-b-P4VP due to the dwelling of the carboxyl group in the backbone of PCDA (Fig. S1). The supramolecular lamellae containing PS-b-P4VP and PCDA moieties could be elaborately produced by retarded evaporation (Scheme 1, panel a) [35]. Upon exposing the as-obtained film to the UV light for a preset period of time, a color conversion from colorless to blue occurs in the film due to the polymerization of PCDA (panel b). Meanwhile, the cross-linking of PS-b-P4VP is available. Then the organic solvents are dropped onto the film surface (panel c). After 30 s, a digital photo of the film is captured instantly regardless of whether the solvents completely evaporate or not. Only the solvents having strong affinities to PS can selectively penetrate into the films and further interact with blue PDA for solvatochromism, leading to a visible blue-to-red transition in the cross-linked supramolecular film (panel d). In stark contrast, the pristine blue color remains in the film in response to the treatments of the solvents with weaker affinities to PS, in which these solvents are not capable of penetrating into the film sufficiently (panel e).
3.2. Demonstration of hydrogen bonds in supramolecules

To demonstrate the formation of hydrogen bonds between PS-b-P4VP and PCDA, FTIR was employed to characterize PS-b-P4VP, PS-b-P4VP(PCDA) and purified PCDA samples (Fig. 1). The new absorption peak at 1012 cm\(^{-1}\), which is merely distinct in the spectrum of PS-b-P4VP(PCDA), indicates the formation of hydrogen bonds between PS-b-P4VP and PCDA [34-38]. The absorption peak of 993 cm\(^{-1}\) represents the free pyridine groups of PS-b-P4VP while it is unavailable in the spectrum of PCDA [38]. Compared to that of PS-b-P4VP, the spectrum of PS-b-P4VP(PCDA) exhibits a weaker absorption peak at 993 cm\(^{-1}\), which is due to the consumption of free pyridines resulting from the formation of hydrogen bonds. As a result of the lower ratio of PCDA/4VP (~0.56), the consumption of free pyridines is incomplete. Hence, the absorption peak of free pyridine groups at 993 cm\(^{-1}\) became weaker rather than vanished in the spectrum of PS-b-P4VP(PCDA).

3.3. Structural characterizations of the supramolecular films

The as-prepared supramolecular film with a thickness of ca. 6 μm is visually transparent. Due to the lower surface energy of PS (γ\(_{PS} = 45.5\) mJ/m\(^2\)) than P4VP (γ\(_{P4VP} = 50\) mJ/m\(^2\)) [39], the preferential segregation of PS on the film surface is inevitably performed in the course of film formation. To demonstrate PS rather than P2VP chains dwelling on the top surface of the film, a water contact angle was measured as 100° on the smooth surface of the film, which is in good consistence with that of PS homopolymers [40].

To investigate the inner structures of the supramolecular film, small-angle X-ray scattering (SAXS) was employed subsequently. From the 1D SAXS profile of the supramolecular film (Fig. 2b), a domain spacing of ca. 50.2 nm was calculated according to the primary peak of q\(^*\) = 0.0125 Å \((d = 2\pi/q^\ast)\). The periodical lamellae of the supramolecular film were demonstrated by the higher-ordered peaks of 3q and 4q [41]. To further observe the lamellar structures, the SEM cross sections of the supramolecular film subjected to ethanol soaking at 50 °C for 3 h were collected (Fig. 2c and d). It should be noted that UV irradiation has not been applied in such supramolecular film prior to swelling, leading to a possibility of disruption of hydrogen bonds as well as dissociation of supramolecular lamellae [35]. That is, hot ethanol could extract PCDA, swell hydrophilic P4VP chains and then plasticize PS chains, thus the PS and P4VP layers should tend to dissociate into independent lamellae in ethanol [42,43]. If the temperature and duration of ethanol soaking are controlled appropriately, lamellae would be slightly deformed rather than dissociated completely followed by dispersed into ethanol [35]. Although the lamellar nanostructures were indeed deformed in the course of ethanol soaking at 50 °C for 3 h, the lamellae morphology was still unambiguously presented in the cross section (Fig. 2d). As the “comb-coil” supramolecular BCPs have been extensively reported by self-assembly of BCPs and amphiphile molecules [31,36,44-48], here the supramolecular lamelle consisting of PS-b-P4VP and PCDA should be in the form of “comb-coil” prior to ethanol soaking (Fig. S2). Such supramolecular structures can construct BCP protective layers for PCDA for further colorimetric sensing.

3.4. Color transition induced by UV irradiation

After the photopolymerization of PCDA by UV irradiation [49], the supramolecular film can be transformed from colorless to blue color with a characteristic absorption peak of around 640 nm due to the extended π-electron conjugation of PDA [15,50]. Here, UV-induced color transition was monitored in the supramolecular film by the visible absorption spectra (Fig. 3). With the extension of UV irradiation (254 nm, 1 mW/cm\(^2\)), the absorption intensity was gradually raised. When the irradiation duration came to 18 min, the absorption intensity approached a maximum value. Meanwhile the supramolecular film exhibited an intense blue color (the inset of Fig. 3). In fact, the blue color was clearly presented in the film when the duration of UV irradiation was designated as 3 min. We also note that a faint color transition was performed while a thinner supramolecular film with UV irradiation of 3 min was used (Fig. S3). Moreover, the fast evaporation of solvent caused a non-uniform film in terms of thickness along the transverse direction, resulting in a heterogeneous color transition (Fig. S4). Such result suggests that the retarded evaporation strategy is vital to the fabrication of high-quality supramolecular films for colorimetric sensing.

3.5. Recognition of organic solvents by supramolecular sensors

PS and P4VP can be cross-linked by UV light [51-53], as a result, the irradiated supramolecular film with lamellar domains possesses the capability of solvent resistance at some extent. Considering that sophisticated procedures were applied in designing protective multilayers for the recognition of organic solvents reported previously [1], we develop a new approach to distinguish organic solvents by selective
penetration of the organic solvents into the supramolecular films. Upon exposed to the tested solvents, tetrahydrofuran (THF), dichloromethane (CH₂Cl₂), chloroform (CH₃Cl), ethyl acetate (EA) and toluene, for 30 s, the films with UV irradiation of 3 min underwent visible blue-to-red transitions (Fig. 4, top). This phenomenon can be illustrated by the difference of polymer-solvent interaction parameters (Supporting Information S5 and Table S1). With the similar PS-/P4VP-solvent interaction parameters, CH₂Cl₂ and CHCl₃ have the homogeneous penetration capability to the cross-linked PS and P4VP domains, which allows them to further interact with PDA [32,54,55]. Surprisingly, THF-, EA- and toluene-treated films also exhibited strong visual blue-to-red color transitions in spite of the weak affinities of these solvents to P4VP, indicative of the large dependence of the color transition on PS rather than P4VP. Moreover, THF is endowed with the excellent colorimetric ability of all [1]. Hence, the UV-treated supramolecular film exposed to THF exhibited the brightest red color compared to other cases. The sensing results illustrate that the cross-linked PS lamellae rather than the cross-linked P4VP domains are the pivotal protective layers in impeding the penetration of organic solvents into the films, which further supports the “comb-coil” structures in the supramolecular films (Fig. S1).

The good miscible properties of acetone with PS and P4VP have been demonstrated by the PS-/P4VP-acetone interaction parameters (< 0.5, Table S1), but the interaction between acetone and PDA is possibly not so strong. Therefore, a blurred blue-to-red transition was observed. Additionally, upon exposed to ethanol, isopropanol (IPA) and hexane, the supramolecular sensors exhibited no blue-to-red transition. The relatively weak affinities of these solvents to PS lead them to penetrate in PS layers insufficiently. It should be noted that the cross-linked supramolecular films have high solvent resistance, thus the films survive the organic solvent tests.

To further recognize the organic solvents and deeply understand the blue-to-red transition, the corresponding confocal fluorescence microscopy images of the films were presented (Fig. 4, middle). It is worth noting that the UV-irradiated photopolymerized PDA merely exposed to the organic solvents have the potential to exhibit fluorescent properties [14]. Treating the films with THF, CH₃Cl₂, CHCl₃, EA and toluene led to the generation of fluorescence, among which the THF-induced one shows the strongest response. This phenomenon is in good agreement with the presentation of the digital photos (Fig. 4, top). Meanwhile, the supramolecular films without the blue-to-red transition presented no fluorescence under confocal fluorescence microscopy [1,14]. In addition, we found that the film exposed to EA was slightly destroyed and collapsed, forming a shallow pit on the surface. The outcome implies an efficient access can be realized in distinguishing EA from the tested organic solvents in our system.

The optical images were further collected to recognize these solvents (Fig. 4, bottom). The film exposed to THF still has the strongest red intensity of all under optical microscope. Considering that a similar red intensity also appeared in the CH₃Cl₂-treated film, THF is not capable of being exclusively recognized among all organic solvents by this
means. However, according to the optical images, it is much easier to distinguish CH₂Cl₂ and CH₃Cl compared to the previous study. Especially, a small part of the supramolecular film treated with acetone exhibited an apparent blue color, resulting in a distinction between acetone and other organic solvents. Such distinction is possibly attributed to the extrusion of blue PDA on the film surface, which is induced by the strong interaction of PS-b-P4VP with acetone. That is, the weak interaction of PDA and acetone is unable to produce an obvious blue-to-red transition although acetone can penetrate into the film. However, the blue PDA was dissolved out by acetone and further dwelled on the film surface. The UV-treated film exposed to IPA also presented a fuzzy blue color. We believe that such sensing course is similar with that of acetone. Attributing to the poorer affinity of PS to IPA than to acetone, less IPA penetrated into the supramolecular film to extract PDA out onto the film surface. The intensity of blue color was weakened consequently.

The UV-irradiation duration was subsequently increased to 18 min to improve the polymerization degree of PCDA as well as the cross-linking degree of PS-b-P4VP. Deeper cross-linking of BCP by extending the UV irradiation will enhance the solvent resistance of the supramolecular films, which makes harder for good solvents to penetrate into the sensors. Differentiation of the organic solvents with a strong affinity to PS is then possibly realized.

The films treated by THF and CH₃Cl still exhibit the visible blue-to-red transition as demonstrated by the digital images (Fig. 5, top). By naked eyes, CH₂Cl₂ and CHCl₃ can be easily differentiated as the film treated with CH₂Cl₂ presents a weaker color transition compared to that of CHCl₃ treatment. Moreover, the difference of the fluorescence intensities between the films treated with CH₂Cl₂ and CHCl₃ also directly illustrates the impurity of the two colorimetric transitions (Fig. 5, middle). Compared to the 3 min-UV irradiated films, however, the supramolecular films with UV irradiation of 18 min exhibited a lighter red color as well as a weaker fluorescence intensity upon exposed to EA and toluene. Additionally, THF and acetone could be recognized according to their unique colorimetric properties by employing an optical microscope (Fig. 5, bottom).

To solely distinguish THF by naked-eyes, the supramolecular films were deliberately UV-irradiated for an excessive duration of 27 min to highly cross-link PS-b-P4VP. In fact, the maximum polymerization of PCDA has almost been achieved by UV irradiation of 18 min (Fig. 3). As expected, the film exposed to THF exhibited an unambiguously visible red color, while the extremely weaker red color or pristine blue remained in the other solvents-treated films (Fig. 6). The apparent blue-to-red transition resulted in a visual differentiation of THF among the diverse organic solvents in our system.

3.6. Controlled nonvisualization and revisualization of the imprint by incorporating thermochromism and solvatochromism

As displayed in Fig. 7, the supramolecular film has a blue color after illumination with UV light for 3 min. Upon heated at 100 °C for 3 min, the blue PDA should be transformed into red ones [56]. The heated supramolecular film exhibited a visible blue-to-red color transition as expected (the inset in Fig. 7). Meanwhile, the absorption peak is accordingly shifted from 640 to 540 nm. To exploit applications of the supramolecular sensors based on the color transition of PDA, we then incorporated such thermochromism with solvatochromism to develop a straightforward technique to realize the nonvisualization of an imprint followed by its revisualization.

We employed 50 μL IPA as the ink, which were then dropped onto the surface of the 3 min-irradiated supramolecular film. A visible imprint could be clearly observed on a blue background after evaporation
of IPA (Fig. S6a). Subsequently, the film was heated at 100 °C for 3 min to convert its blue color to a red one (Fig. S6b). The imprint was too blurry to be distinguished (nonvisualization) induced by the blue-to-red transition. We speculated that IPA could mildly destroy and further penetrate into PS lamellae (the weak affinity of IPA to PS as determined from Fig. 4). Subsequently, PDA phases were extracted out on the film surface (the strong affinity of IPA to P4VP, Table S1). Besides, the polymer chains are endowed with high mobile ability at elevated temperatures as a result of the low glass transition temperature of PS of polymer chains are endowed with high mobile ability at elevated temperatures. Therefore, the slightly disrupted film surface can be recovered upon heating. We note that the integrity of PS lamellae is the pivotal factor to realize the nonvisualization of the imprint. For instance, the nonvisualization can not be realized by employing some organic solvents with good affinities to PS (Fig. S7). To enable the imprint to be revisualized on the film surface, the supramolecular film was irradiated by UV light for 3 min again (Fig. S6c). Then an outline appeared, leading to a clearer imprint than before (revisualization). The imprint was irradiated by UV light for 3 min again (Fig. S6c). Then an outline appeared, leading to a clearer imprint than before (revisualization). The outline should be determined to be the blue PDA as PS-b-P4VP is colorless, which is in accordance with the aforementioned analysis that IPA extracts PDA out. The fluorescence image of the film was further collected. As blue PDA phases have no fluorescence, the fluorescence-defect outline of the imprint should be consisted of blue PDA (Fig. S6d). Such a straightforward process has much potential to be used in code protection and other fields.

4. Conclusions

Supramolecular PS-b-P4VP(PCDA) films consisting of the alternating stacked PS and P4VP(PCDA) layers are produced by retarded evaporation. The PCDA phases can be facilely photopolymerized to yield blue PDA under UV light, while the cross-linking of PS-b-P4VP occurs. With the elongation of the irradiation duration, the polymerization of PCDA as well as the cross-linking of PS-b-P4VP is gradually enhanced. Attributing to the intrinsic protection of PDA by the cross-linked supramolecular lamelle, the specific organic solvents are capable of penetrating into the films and further interacting with PDA, inducing a visible blue-to-red transition. The differentiation of common organic solvents is thus accessible. Furthermore, a straightforward technique to realize the nonvisualization of an imprint followed by its revisualization is developed by incorporating thermochromism with solvatochromism. The developed supramolecular lamelle provide an innovative yet simple approach to prepare solvatochromic sensors.

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Appendix A. Supplementary data

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References


