ORIGINAL ARTICLE

Effect of π–π interaction-induced secondary doping on the gold-like luster of oligo(3-methoxythiophene) cast films

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Abstract

We herein investigated the effect of benzene contact treatments on the preparation of solution-cast gold-like lustrous films of doped oligo(3-methoxythiophene) (weight-average degree of polymerization = 21). More specifically, benzene contact treatments involving the addition of benzene and benzene exposure were employed. In the former case, benzene was added to a nitromethane coating solution, and the resulting solution was applied to a glass plate to form a film. Compared with the original film, the resulting film exhibited a higher luster and more intense yellowness when 2.0 wt% benzene was added to the coating solutions. In the latter treatment, the original film was exposed to benzene vapor for ≥30 s, which also caused an increase in luster and yellowness. Such a gold-tone-enhancing effect was not observed upon replacing benzene with hexane. Moreover, both benzene contact treatments increased the number of edge-on lamellar crystallites in the film. Based on these results, it was concluded that upon benzene contact treatment, the oligomers adopt a planar conformation in which benzene molecules are sandwiched between the oligomers. These sandwich structures facilitate the formation of edge-on lamellar crystallites, which are the most likely cause of the gold tone.

Introduction

In recent years, conjugated polymer films that exhibit gold, silver, and bronze metallic lusters have received increasing attention [1–8], as these specialized, advanced polymer materials are expected to be applicable in next-generation decorative paints since they do not contain metal flake pigments, unlike current products [9]. The current products are undesirable, as the presence of metal flakes can lead to flake sedimentation in paints, flake corrosion, and heavy film coatings, and their application in ink jet printing is impossible because the nozzles become clogged with the flakes.

To address the above issues, we recently synthesized a ClO_4^--doped 3-methoxythiophene oligomer (O3MeOT, weight-average degree of polymerization = 21) and found that gold-like lustrous films were formed on a glass plate following the application of a nitromethane solution of O3MeOT [10]. The development of this gold-like luster was attributed to the spontaneous formation of lamellar structures. The key lamellar structures are the edge-on and face-on lamellar crystallites in films [10]. In the former and latter crystallites, thiophene rings are aligned perpendicular and parallel to the substrate, respectively. Higher values of the refractive index (n) and extinction coefficient (κ) were exhibited by the edge-on lamella-dominant film than by the face-on lamella-dominant film when the incident light beam was normal to the film surface, leading to the development of higher luster by the former film [11]. In addition, O3MeOT exhibits intense light absorption above ~570 nm and hence has a blue to purple color. Therefore, the edge-on lamella-dominant film shows a lustrous color complementary to blue-purple, i.e., a lustrous gold-like color. Moreover, we demonstrated that the O3MeOT dimer (π-dimer) present in the nitromethane coating solution contributed significantly to the development of the luster [12].

Wu et al. prepared doped polythiophenes bearing various long alkyl chains and allowed the resulting films to contact

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solvent vapor for 30 s [13]. Their results suggested that the thiophene rings were stacked in parallel with one another in such a way that upon exposure to benzene vapor, the benzene molecules were sandwiched between the thiophene rings. This orientation induced an increase in the absorption owing to the bipolaron band and enhanced the crystallinity and the electrical conductivity of the films; thus, benzene was referred to as a second dopant.

On the basis of these findings, we expect that more highly lustrous gold-like films could be obtained by using benzene as a second dopant, as the supramolecular interactions between the O3MeOT molecules may be enhanced upon benzene exposure to yield greater quantities of edge-on lamellar crystallites. Thus, we herein examine the film properties (luster, color, and molecular orientation) of O3MeOT films upon exposure to benzene vapor. Furthermore, we also investigate the solution and film properties upon addition of benzene to the nitromethane coating solution of O3MeOT.

Experimental

Materials

3-Methoxythiophene (>98%) was purchased from Wako Pure Chemical Industries, Osaka, Japan. $Fe(ClO_4)_3 \cdot nH_2O$ (with an anhydride content of 70.7%; Wako Pure Chemical Industries) was used as the oxidizing agent for the oligomerization of 3-methoxythiophene. Acetonitrile (>99.7%, Kanto Chemical, Tokyo Japan), nitromethane (>98.0%, Tokyo Chemical Industry, Tokyo Japan), benzene (>99.5%, Kanto Chemical), and hexane (>96.0%, Kanto Chemical) were used as supplied. The glass plate (S1225, Matsunami Glass, Osaka Japan) was cleaned by sonication in acetone for 10 min prior to use. O3MeOT was prepared according to a previously reported method [10]. Its polymerization degree was determined to be 21 by gel permeation chromatography using a Jasco RI-2031 Plus (Jasco, Tokyo, Japan) equipped with a Hitachi UV-4200 (Hitachi, Tokyo, Japan) and two Shodex KF-806M columns (Showa Denko, Tokyo, Japan). Electron dispersive X-ray (EDX, JSM-6510A, JEOL, Tokyo Japan) analysis revealed a doping level of 25%, defined as the number of ClO_4^- ions per 3-methoxythiophene unit.

Preparation of the coating solutions and the films

A typical coating solution was prepared by dissolving O3MeOT (0.010 g) in nitromethane (0.99 g, 0.87 mL) and stirring for 90 min at 22 °C. Benzene (1, 5, or 10 drops, 1 drop = 0.020 g) was then added to the coating solution as required. The films were subsequently prepared on a glass plate (15 × 25 mm × 1.1 mm) by application of the coating solution and drying in an ambient atmosphere. The quantity of the applied coating solution was adjusted to 0.14 g.

Benzene (or hexane) exposure test method

Exposure of the coating films to benzene (or hexane) vapor was carried out at 22 °C as follows. A portion of the desired solvent (40 mL) was placed in a 100 mL beaker, and the coating film was placed 15 mm above and in parallel to the liquid surface.

Characterization of the films and coating solutions

Following the dissolution of O3MeOT in nitromethane or nitromethane/benzene, the resulting solutions were characterized by UV-vis absorption spectroscopy (U-3000 spectrophotometer, Hitachi) and viscosity measurements (LVDV-II + PCP cone and plate rotoviscometer, Brookfield Eng. Lab, Middleboro, MA, USA). For the viscosity measurements, the temperature was maintained at 25.0 °C by circulating thermostated water (Cooling Thermo Pump CTP-101, EYELA, Tokyo Japan) around a jacketed vessel containing the test solution. UV-vis reflection spectra were obtained using a Jasco MSV-379 spectrometer (Jasco) with incident and reflection angles of 23° from the vertical position. The spectra were recorded at 23 °C using an evaporated aluminum film as the reference material. The films were observed using an optical microscope (VHX-5000, KEYENCE, Osaka, Japan), and the film color was analyzed using a CM-600d spectrophotometer (Konica Minolta, Tokyo, Japan) with a D65 illuminant and an observer angle of 10° (CIE 1964 Standard Observer). The CIELab parameters were $a*$ for redness-greenness, $b*$ for yellowness-blueness, and $L*$ for lightness (black-white). Out-of-plane X-ray diffraction (XRD) measurements were performed using a diffractometer (X'Pert MRD, Malvern Panalytical, Malvern, UK) equipped with a CuKα source in 2θ scan mode at a fixed incident angle of 1.0°. The film thickness, t, and root mean square surface roughness, R_q, were measured using a surface profile measuring system (model Dektak 3030, Sloan, now Veeco, Plainview, NY, USA). A metallic gold film (0.20 μm thick) was deposited on a glass plate using a vacuum evaporation method.

Results and discussion

Comparison of the various benzene treatment methods

As described in the introduction section, Wu et al. demonstrated that the regularity of polyalkylthiophene
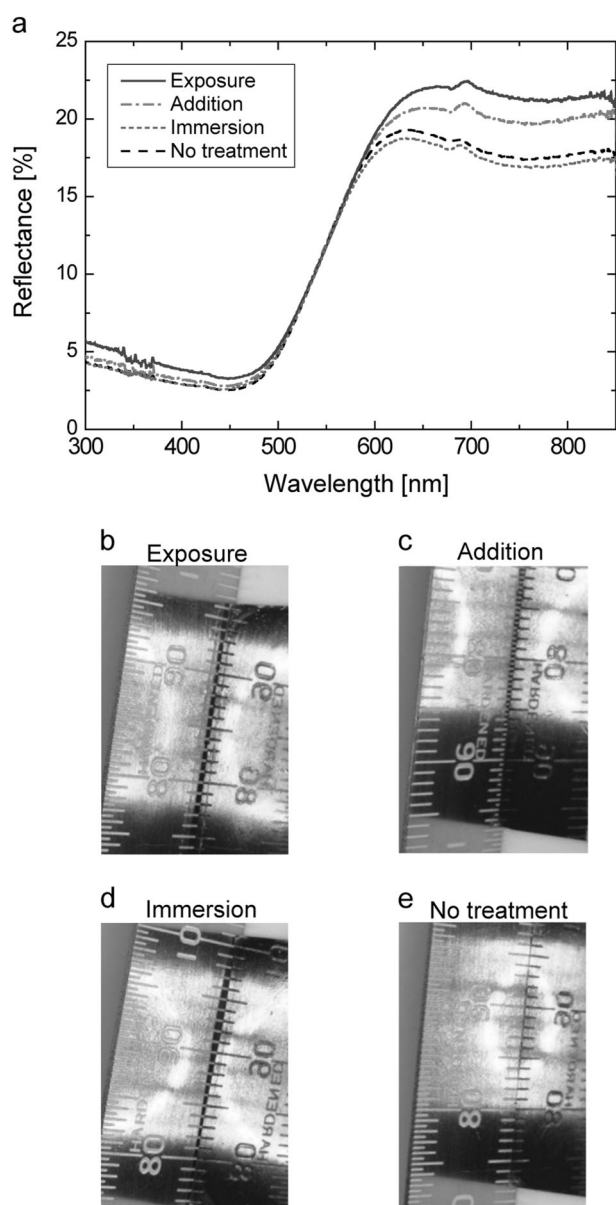
Fig. 1 a Specular reflection spectra of the O3MeOT films subjected to benzene exposure treatment, benzene addition treatment, and benzene immersion treatment. For comparison, a spectrum of the untreated film (i.e., the as-prepared film) is also included. **b–e** Digital microscopy images of the O3MeOT films of the spectra from Part (**a**)

stacking structures was improved by exposing their films to benzene vapor for 30 s [13]. Based on this finding, we subjected the O3MeOT films to benzene contact treatments involving exposure of the films to benzene vapor (see Experimental section, benzene exposure treatment), the addition of a single drop (0.020 g) of benzene to the coating solution and uniform mixing by stirring prior to film formation (benzene addition treatment), and immersion of the film in benzene for 30 s (benzene submersion treatment).

Thus, Fig. 1a shows the specular reflection spectra obtained for the films subjected to the abovementioned three treatments.

For comparison purposes, the spectrum of an untreated film (film°) is also included. As indicated, all films showed a rapid increase in their reflectance at ~480 nm. The reflectance values in the regions of the yellow (570–590 nm), orange (590–620 nm), and red (620–750 nm) wavelengths were significantly higher than those in the regions of the purple (380–450 nm) and blue (450–495 nm) wavelengths, as is the case for the vacuum-evaporated gold film, resulting in gold-like coloration. In addition, digital microscopy images of the films corresponding to the spectra in Fig. 1a are shown in Fig. 1b–e, where their luster was clearly demonstrated by the reflection of the metal ruler positioned perpendicular to the film. Although differences in the reflection characteristics could not be clearly distinguished from these images, the data in Fig. 1a confirm that there is a reflectance difference of several percent. Furthermore, the specular reflection values greater than ~600 nm increased in the order of no treatment (as-prepared) ≈ submersion treatment < addition treatment < exposure treatment. This indicates that the benzene exposure treatment is the most effective method for enhancing the gold-like luster. Based on this result, no further investigation of the benzene submersion treatment was carried out, as this treatment resulted in no significant improvement in the lustrous properties. Moreover, Fig. 2 shows the results of the hue/saturation measurements (i.e., the a^* and b^* values). Regardless of the treatment method employed, the b^* value of the film was increased relative to that of the untreated film (i.e., an increase in yellowness) following contact with benzene. In contrast, the a^* value remained relatively constant. In Fig. 2, a plot point for metallic gold is also included, whereby it is apparent that the coating films have more reddish hue than metallic gold; thus, to achieve a hue/saturation of the coating films similar to that of metallic gold, their redness value must be reduced.

In our previous study [12], it was demonstrated that improvements in reflectance and in the b^* value were associated with the quantity of edge-on lamellar crystallites, with higher quantities of crystallites giving a higher luster and an increased yellowness. However, it should be noted that polyalkylthiophenes are semicrystalline polymers that possess crystal domains surrounded by amorphous regions [14–21]. In this material, the crystalline domains are composed of an orthorhombic unit cell with lattice parameters a (separation of the main chain stacks), b (stacking distance of the main chains), and c (repetition distance along the main chains). Our previous report also demonstrated that the crystal domains of O3MeOT have a structure similar to those of polythiophenes [10–12]. The XRD pattern of the cast O3MeOT film exhibited peaks at $2\theta = 7.84$, 15.84, and 25.11°, where the peaks at 7.84 and 15.84° represent the crystallographic (100) and (200) reflections, respectively, thereby confirming the layered structure of the lamellae, as shown in Fig. 3a. The lamellar interlayer spacing was determined to be 1.13 nm from the dominant first-order reflection at $2\theta = 7.84°$, while the peak at

$2\theta = 25.11°$ corresponding to the (020) reflection associated with π–π stacking of the O3MeOT chains provided the interchain distance between the π-stacking oxidized chains
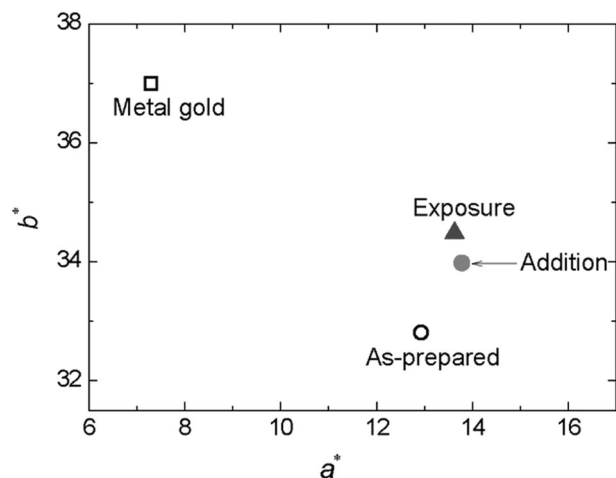

Fig. 2 The a^* and b^* values of the films subjected to benzene exposure treatment (▲), benzene addition treatment (●), and no treatment (as-prepared, ○) shown in Fig. 1a. The plot point of an evaporated metallic gold film is also included (□)

(i.e., 0.35 nm). Considering that the XRD measurements were carried out in the out-of-plane mode, which is sensitive to the lattice parameter in the film thickness direction, the signals at $2\theta = 7.84$ and $15.84°$ confirm the presence of edge-on lamellar crystallites (Fig. 3b), and the signal at $2\theta = 25.11°$ indicates the presence of face-on lamellar crystallites (Fig. 3c).

We then examined the effect of the benzene contact treatments on film crystallinity through XRD measurements. Thus, Fig. 4 shows the out-of-plane XRD patterns of the O3MeOT films subjected to benzene exposure treatment for 30 s (a), benzene addition treatment (b), and no treatment (c, film°). All patterns gave peaks at $2\theta = 8.01$, 15.71, and 24.6°, corresponding to the (100), (200), and (020) reflections, respectively. The dominance of the (100) peak indicated that the crystallites were preferentially oriented with the (100) axis normal to the film and the (020) axis parallel to the film, indicating that the lamellae preferentially adopted an orientation parallel to the glass plate (Fig. 3b, edge-on orientation). In addition, the highest peak intensity at $2\theta = 8.01°$ was observed for the exposure treatment (Fig. 4, pattern a) followed by the addition treatment (Fig. 4, pattern b), whereas the lowest peak intensity was observed for the untreated film (Fig. 4, pattern c). Although the difference was small, this
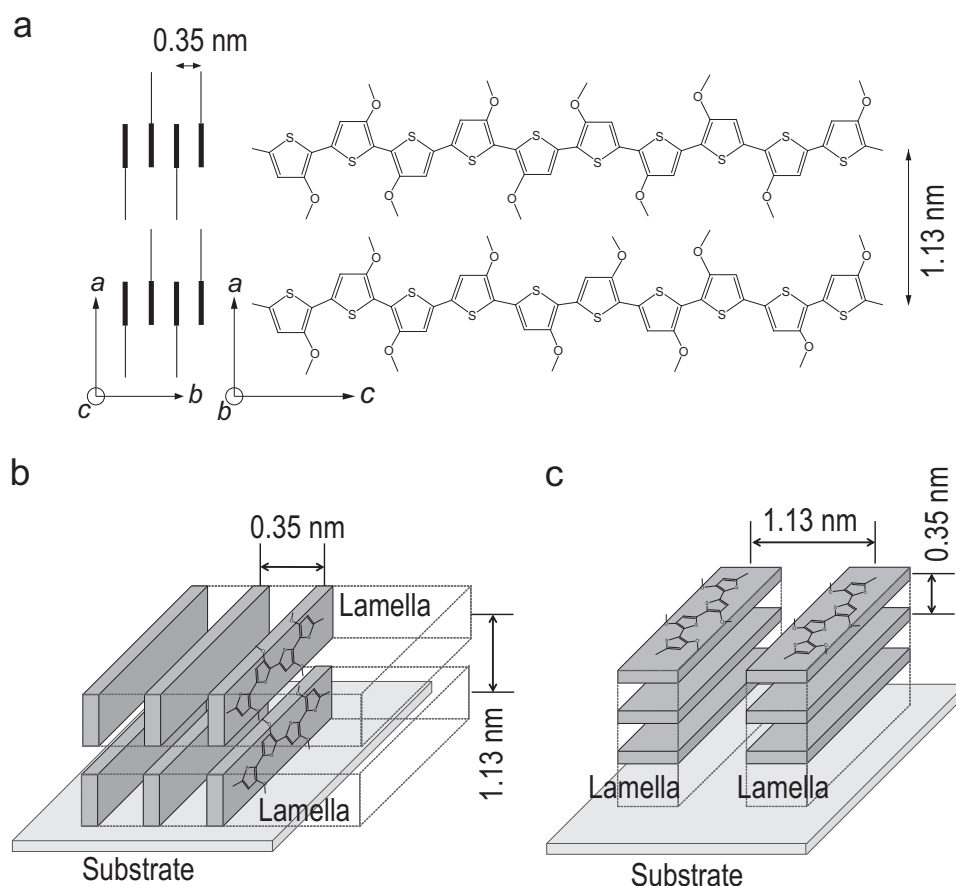
Fig. 3 a Schematic representation of the molecular arrangement of the oligomer. **b** The edge-on lamellar structure. (**c**) The face-on lamellar structure
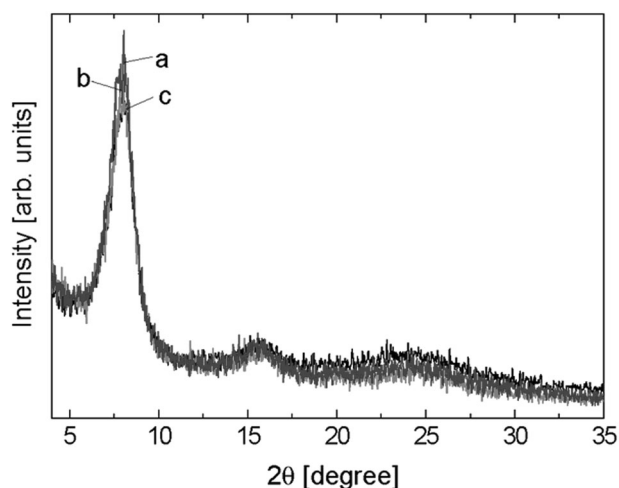
Fig. 4 X-ray diffraction (XRD) patterns of the films: (**a**) benzene exposure treatment for 30 s, (**b**) benzene addition treatment, and (**c**) no treatment

order of peak intensity was reproducible. These results correlate with the film reflectance data shown in Fig. 1a, thereby supporting our explanation that the gold-like luster is caused by the presence of edge-on lamellar crystallites. Previously, we electrochemically synthesized an O3MeOT film in which face-on lamellar crystallites were dominant in the crystal domains [11]. This film was characterized by its purple hue and low reflectance. It is therefore likely that the enhancement in the relative ratio of the edge-on structure ($2\theta = 8.01°$) to the face-on structure ($2\theta = 24.6°$) leads to the formation of a yellow emphasis film, i.e., an increase in $b*$ as shown in Fig. 2, as purple is a complementary color of yellow.

Moreover, the color of the film is associated with the film thickness. The film exhibited a blue color when its thickness was below a few hundred nanometers, but beyond this thickness, its color changed from blue to gold. To understand the effect of the film thickness, we initiated research on the determination of the molecular packing of the thin and thick oligomer films by NEXAFS (near-edge X-ray absorption fine structure) spectroscopy, and the results will be reported elsewhere in the near future.

We also investigated the effect of toluene contact treatments (addition, exposure, and submersion treatments) on the spectral reflection characteristics of films in a manner similar to the benzene contact treatments. The results showed the same trend as the results of the benzene treatments, although the reflectance change was small (Supplementary Figure S1).

## Detailed investigation into the benzene addition treatment

Following confirmation of the effectiveness of the benzene addition treatment (see the previous section), we examined the influence of the quantity of added benzene. Thus, coating solutions were prepared by adding one drop (coating solution 1), five drops (coating solution 5), or ten drops (coating solution 10) of benzene to the typical coating solution (see Experimental section). It should be noted that although O3MeOT was insoluble in benzene, no precipitation occurred in the coating solutions. Fig. 5a shows the specular reflection spectra of the films prepared from coating solutions 1 (film 1), 5 (film 5), and 10 (film 10) along with the spectrum of film°. As described in the previous section, the reflectance was found to increase upon the addition of a single drop of benzene; however, the addition of five or ten drops caused a significant decrease in reflectance and resulted in the formation of brown films with poor luster. Moreover, color measurements (Fig. 5b) demonstrated that the yellowness ($b*$ value) was increased by the addition of a single drop of benzene but significantly decreased upon the addition of five or ten drops.

To identify the origins of the abovementioned reflectance and color changes, visible absorption spectra and viscosity measurements were carried out on the coating solutions. Thus, Fig. 6a shows the visible absorption spectra of the solutions obtained by diluting the coating solutions 1000 times by weight. It should be noted that the concentrations of O3MeOT in the coating solutions differed due to the addition of different quantities of benzene. More specifically, the O3MeOT concentrations in the typical coating solution and in coating solutions 1, 5, and 10 were 3.9, 3.7, 3.5, and 3.1 mM, respectively. These values were calculated using the average molecular weight, the doping level, and the quantity of added benzene. In addition, the molar absorption coefficient, ε, calculated from the absorbance at 769 nm, is shown in Fig. 6b as a function of the quantity of added benzene. As indicated, the value of ε was greatly reduced by the addition of a single drop of benzene, and subsequently, it gradually decreased as the number of drops was increased. This was attributed to the hyperchromic effect, in which the molar absorption coefficient of a solution of chromophores is smaller in the aggregation or association state than in the isolated dissolution state [22–25]. Thus, the result presented in Fig. 6b suggests the formation and growth of O3MeOT aggregates upon benzene addition.

To confirm such aggregate formation, viscosity (η) measurements were carried out. Fig. 7 shows the relationship between η and the shear rate (γ) for coating solutions 1 (a), 5 (b), and 10 (c) and for the typical coating solution (d). At a fixed shear rate, η increased upon the addition of one or five drops of benzene. The typical coating solution and coating solution 1 both exhibited Newtonian fluid properties, while coating solution 5 exhibited pseudoplastic properties. It is generally accepted that the intrinsic viscosity [η] of a polymer solution is related to the viscosity average polymer molecular weight, M_v, according to the Mark-Houwink-Sakurada
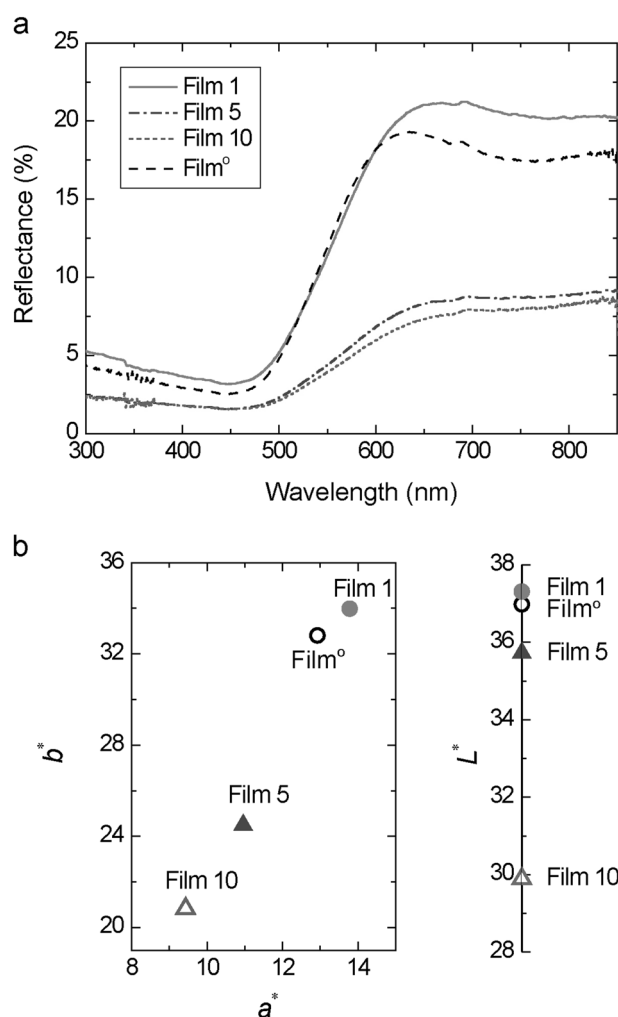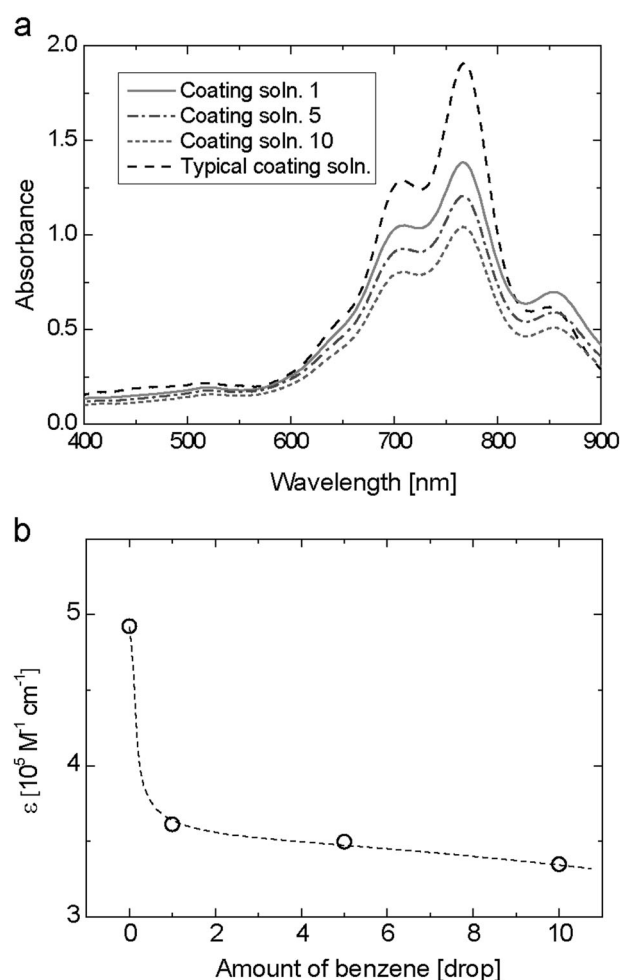
Fig. 5 **a** Specular reflection spectra of the O3MeOT films prepared from coating solutions 1, 5, and 10. For comparison, the spectrum of the untreated film is also shown. **b** The a^*, b^*, and L^* values of film 1 (●), film 5 (▲), film 10 (Δ), and film° (○). t: film 1, 1.1 μm; film 5, 4.1 μm; film 10, 3.0 μm; film°, 1.2 μm. R_q: film 1, 0.024; film 5, 0.39; film 10, 0.76; film°, 0.026

Fig. 6 **a** Visible absorption spectra of 1000-fold diluted solutions of coating solutions 1, 5, and 10 and of the typical coating solution. **b** Dependence of the molar absorption coefficient, ε, on the quantity of benzene added

equation [26–28]:

$$[\eta] = KM_v^a,$$

where K and a are constants for a given solute-solvent system. Based on this relationship, the increase in η with the addition of one and five drops of benzene suggests an increase in the apparent molecular weight of the dissolved species. More importantly, the value of η for coating solution 1 was in good agreement with that for the nitromethane solution of an O3MeOT π-dimer [12]. These results indicate that the addition of one drop of benzene induces the formation of the O3MeOT π-dimer-dominant solution, which provides films with a high luster. In contrast, the addition of five drops may lead to the formation of higher-order molecular aggregates, i.e., π-

stacks, which provide films with slightly less luster. These results are compatible with the main conclusion of our previous report [12], where we note that the greatest quantity of edge-on lamellar crystallites in the film were formed from the π-dimer-dominant solution, whereas smaller quantities resulted from the non-aggregated species/π-dimer- and π-dimer-/π-stack-containing oligomer solutions. In Fig. 7, the η value for coating solution 10 was the lowest, which may be explained by the reduction in viscosity through the diluting effect. As indicated in the caption of Fig. 5, the values of t and R_q for films 5 and 10 are significantly larger than those for film 1 and film°. This difference can be accounted for by considering the formation of higher-order aggregates in coating solutions 5 and 10, which leads to an increase in the surface roughness and the apparent film thickness. This result supports the presence of higher-order aggregates in coating
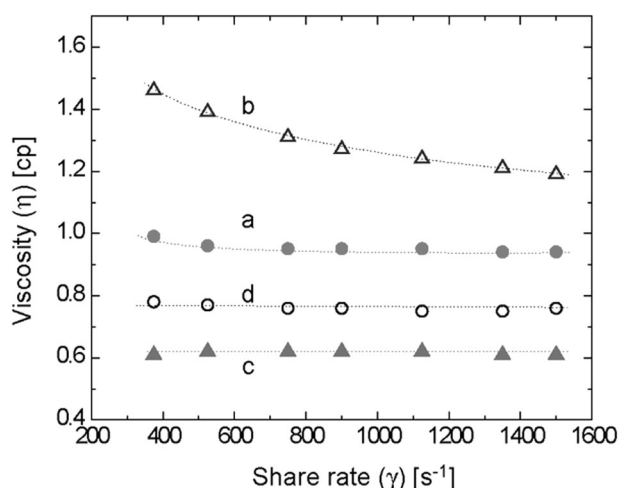
Fig. 7 Dependence of η on γ for coating solutions (**a**) 1, (**b**) 5, and (**c**) 10 and for (**d**) the typical coating solution

Fig. 8 XRD patterns of films (**a**) 1, (**b**) 5, and (**c**) 10

solutions 5 and 10. Additionally, note that the R_q values of film 1 and film° were nearly the same, indicating that the addition of a drop of benzene has little effect on R_q.

Figure 8 shows the XRD patterns of films 1 (a), 5 (b), and 10 (c), where the peak intensity at $2\theta = 8.01°$ increases in the order of film 10 < film 5 < film 1. This result agrees with the order of film reflectance presented in Fig. 5a and suggests that the gold-like luster is indeed caused by the presence of edge-on lamellar crystallites.

Detailed investigation into the benzene exposure treatment

We then examined the effect of the benzene exposure time, where Fig. 9 shows the reflection spectra of the films exposed to benzene vapor for 30 s (a, $film_{ex}B30$) and 300 s (b, $film_{ex}B300$). Spectrum c corresponds to film°. As indicated, the reflectance was enhanced following benzene exposure treatment but appeared to be independent of the exposure time, thereby indicating that a 30 s exposure time is sufficient to improve the reflectance. The XRD patterns of $film_{ex}B30$, $film_{ex}B300$, and film° are shown in Fig. 10, where the peak intensity at $2\theta = 8.01°$ increases in the order of film° < $film_{ex}B300 \approx film_{ex}B30$, which is the same trend observed for the reflectance values presented in Fig. 9. This result again demonstrates that the film luster originates from the edge-on lamellar crystallites. We also carried out measurements of R_q values for $film_{ex}B30$ and $film_{ex}B300$ by the stylus method. As a result, the R_q values of the former and latter films were determined to be 0.021 and 0.029, respectively. These values were also nearly equal to that of film°, and therefore, it can be concluded that the benzene vapor annealing has little effect on the smoothness of a film surface and, in turn, the reflection of gold-like luster.
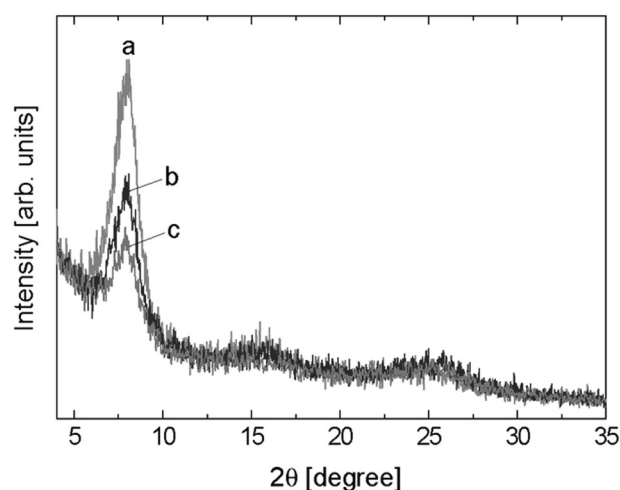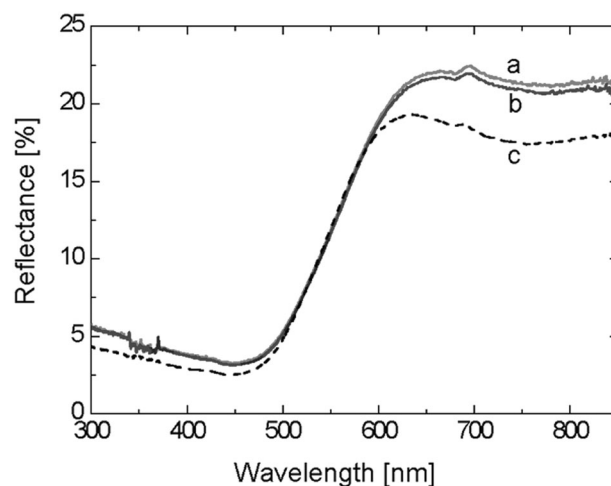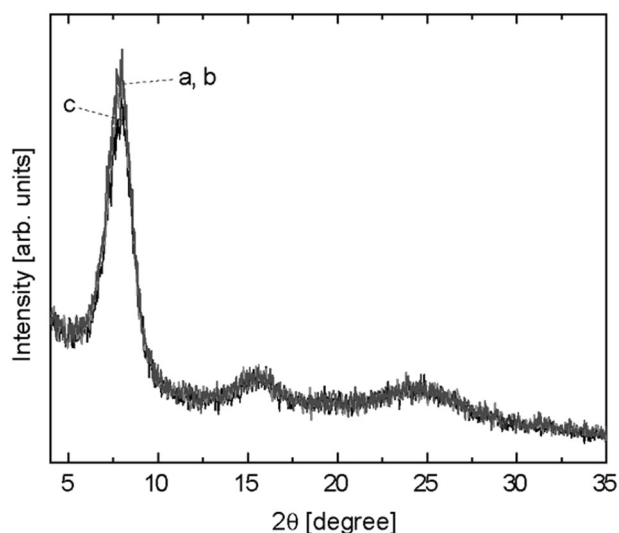

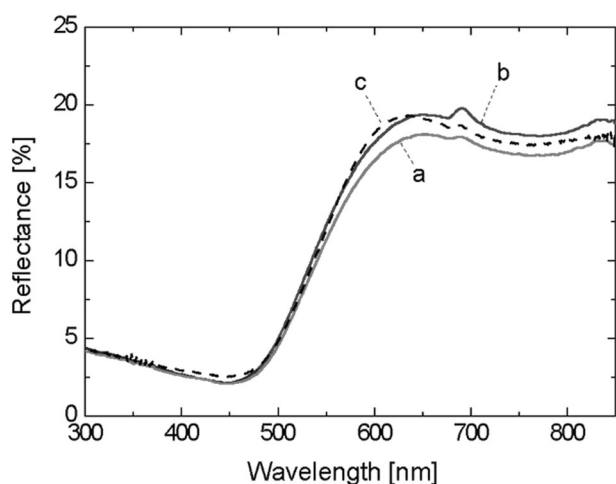Fig. 9 Specular reflection spectra of (**a**) $film_{ex}B30$, (**b**) $film_{ex}B300$, and (**c**) film°

To investigate whether the above reflectance-enhancing effect occurs when using an aliphatic hydrocarbon-based solvent, hexane exposure treatment was examined in a similar manner. Thus, Fig. 11 shows the specular reflection spectra of films exposed to hexane vapor for 300 s (a, $film_{ex}H300$) and 3600 s (b, $film_{ex}H3600$) along with the spectrum of film° (c). In contrast to the spectra obtained after benzene exposure, all spectra obtained after hexane exposure were of similar shapes and intensities, thereby indicating that hexane does not enhance the reflectance. This was also supported by the XRD results presented in Fig. 12. Indeed, Wu et al. previously reported that hexane has no secondary dopant effect on either polytetradecylthiophene or polyoctylthiophene [13].

Fig. 10 XRD patterns of (**a**) film$_{ex}$B30, (**b**) film$_{ex}$B300, and (**c**) film°
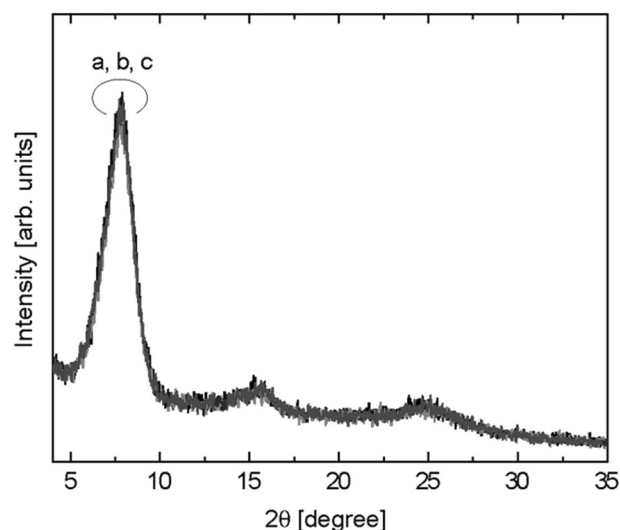
Fig. 12 XRD patterns of (**a**) film$_{ex}$H300, (**b**) film$_{ex}$H3600, and (**c**) film°

Fig. 11 Specular reflection spectra of (**a**) film$_{ex}$H300, (**b**) film$_{ex}$H3600, and (**c**) film°

The above findings therefore suggest that the effects of benzene exposure can be attributed to the π–π interactions between benzene and O3MeOT. More specifically, benzene appears to change the conformation in the amorphous region of the O3MeOT film from coils to more expanded chains through the formation of π–π interactions between benzene and the thiophene rings according to the model described in the literature [13], which in turn facilitates the formation of edge-on lamellar crystallites.

Conclusions

We herein reported the preparation of a 3-methoxythiophene oligomer by oxidative polymerization followed by the application of its coating solution to a glass plate to provide a gold-like lustrous film. During this process, benzene, which is a known secondary dopant to polyalkylthiophenes, was added to the oligomer coating solution prior to film formation (benzene addition). We also examined the effect of benzene exposure treatment by exposing the original film to benzene vapor. Interestingly, both treatments provided films with a higher luster and yellowness than observed in the original film, i.e., an enhanced gold tone. Further investigation revealed that the addition of small amounts of benzene (i.e., 0.020 g per 1.00 g of coating solution) effectively enhanced the gold tone, while the addition of larger amounts (i.e., 0.10 or 0.20 g per 1.00 g of coating solution) reduced the luster and resulted in yellow-brown films. In the former case, the quantity of edge-on lamellar crystallites was larger than that in the original film, while reduced amounts of these lamellar crystallites were detected in the latter film. Moreover, we found that a short exposure time to benzene (30 s) also enhanced the gold tone, with further increases in exposure time having no significant effect. X-ray diffraction measurements once again showed an increase in the amount of the edge-on lamellar crystallites following benzene exposure treatment. For comparison, hexane exposure treatment was performed on the original film; however, no enhancement in the gold tone or in the quantity of edge-on lamellar crystallites was observed. Based on our results, we proposed that following the addition of benzene, two oligomers are brought face-to-face to give benzene-containing π-dimeric structures that facilitate formation of the edge-on lamellar crystallites and should contribute to the enhancement of the gold-like tone of the film. In the case of benzene exposure, benzene molecules may penetrate into the amorphous region of the film and become intercalated between the oligomers. This intercalation would change the oligomer conformation from a coil to an expanded planar structure

through π–π interactions between benzene and the thiophene rings, leading to an increase in the quantity of edge-on lamellar crystallites and, in turn, an enhancement in the gold tone. Our results are of importance, as our demonstrated improvement of the regular orientation of relatively high-molecular-weight compounds should contribute to the supramolecular design of organic polymer materials, i.e., the design of organic polymer electronic devices such as solar cells, light-emitting diodes, and field-effect transistors, whose performances are known to be improved by enhancing the molecular orientation.

Compliance with ethical standards

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