

Preparation and Characterization of Green Reflective Films of Polyaniline Analogs Containing Azobenzene Units

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ABSTRACT: Pd-catalyzed polycondensation of aniline derivatives and 4,4'-dibromoazobenzene affords polyaniline analogs containing azobenzene units. The polymers are red in solution and in thin films state, whereas they have a green luster in thick films. Substitution of 4,4'-dibromoazobenzene for 4,4'-dibromostilbene changes the reflection color from green to blue, whereas the introduction of a non-conjugated unit slightly affects the reflection color. The glossiness of the film is dependent on the smoothness of the film surface. The reflectance measurements using polarized light reveal that reflection spectra correlate well with the complex refractive index ($\tilde{n} = n + ik$) of the film. These results confirm that the green luster can be attributed to the uniform surface reflection of the object, which has a large refractive index and absorption coefficient at around 500 nm. The polymer films exhibit good transmission of radio frequency signals owing to the lack of free electron carriers. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41275.

KEYWORDS: films; coatings; dyes/pigments; optical properties; polycondensation

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INTRODUCTION

Colored surfaces with metallic luster are widely employed in industrial products such as automobiles and household electric appliances because of their luxurious finish. Generally, silver lustrous paints are made by blending aluminum platelets with a polymer,¹ while colored surfaces with a metallic luster are prepared by coating a glossy metal surface with a polymer film containing pigment particles.^{2,3} A representative method for preparing colored reflective films is the preparation of multilayered films consisting of a highly refractive polymer and less refractive polymer^{4–8}; when the layers have regular intervals, the film exhibits a specific color of reflection due to the interference of light, which is called the structural color. Since the films do not contain metal, they can transmit electromagnetic waves*. Alternatively, we previously reported that polyaniline analogs containing azobenzene units are red in solution and in thin-

films, whereas they exhibit a green luster in thick films.⁹ These observations prompted our interest in the origin of the green luster and the ability to tune the reflection color of the films; this protocol would provide a new method for preparing colored reflective films and paints. To prove this concept, a series of polyaniline analog films containing azobenzene and stilbene units were prepared, and optical measurements of the films, including reflectance measurements using polarized light, were conducted. We herein report the preparation and optical characterization of these films. Parts of these results have been reported in a previous communication.⁹

EXPERIMENTAL

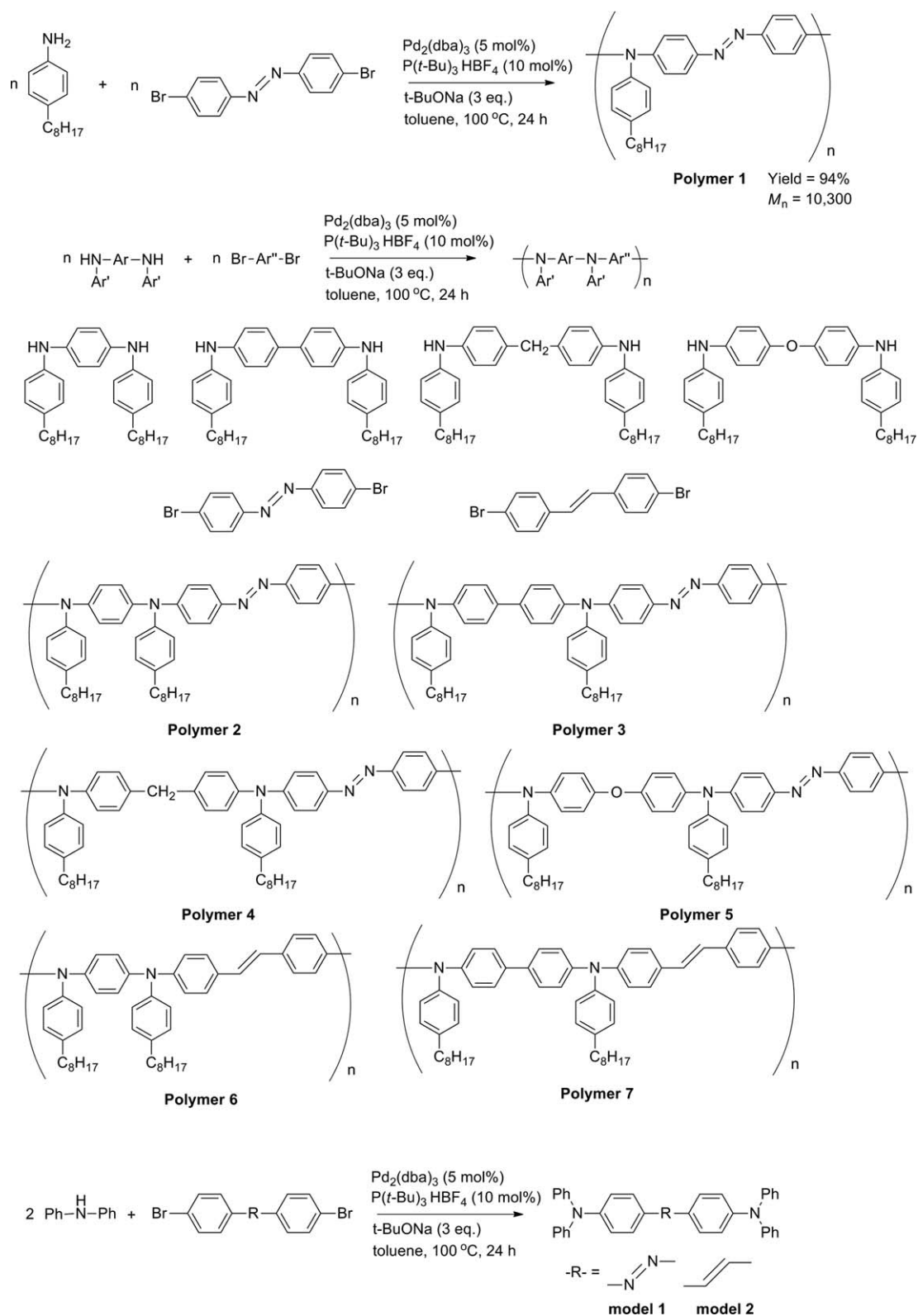
Materials

p-Dibromobenzene, 4-*n*-octylaniline, 4,4'-dibromo-*trans*-stilbene, Pd₂(dba)₃, P(*t*-Bu)₃-HBF₄, and other chemicals were used as received from commercial suppliers. Dehydrated toluene was purchased from Kanto Chemical and used as a dry solvent. 4,4'-Dibromoazobenzene¹⁰ and *N,N'*-bis(4-octylphenyl)-1,4-phenylenediamine⁹ were prepared in accordance with the previous literatures.

*A metal-free film with metallic sheen was developed by Toray Industries Inc.: http://www.toray.com/business/products/plastics/films/fil_012.html and <http://www.toray.jp/films/en/printing/product/picasus.html>.

Additional Supporting Information may be found in the online version of this article.

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Scheme 1. Synthesis of polyaniline analogs and model compounds.

Table I. Results of Synthesis and Optical Properties of Polymers 1–7 and Model Compounds 1 and 2

	Synthetic results			Absorption			Reflection λ_{\max} (nm)
	Yield ^c (%)	M_n ^d	M_w/M_n ^d	Solution ^a		Thin film ^b	
				λ_{\max} (nm)	ϵ (L mol ⁻¹ cm ⁻¹)	λ_{\max} (nm)	
Polymer 1 ^e	94	10,300	3.6	515	23,700	510, 541 ^f	559, 518 ^f
Polymer 2 ^e	98	22,100	1.5	501	29,300	490	543
Polymer 3	99	44,000	3.7	493	30,200	484	530
Polymer 4	97	15,000	4.7	481	33,100	478	520
Polymer 5	99	13,200	3.2	483	33,700	478	516
Polymer 6	93	12,800	2.1	402	22,700	409	442
Polymer 7	89	16,000	1.7	406	34,000	410	442
Model 1 ^g	82	-	-	458	30,600	-	-
Model 2 ^h	91	-	-	389	50,400	-	-

^a In CHCl₃.^b The thin films and the thick films were fabricated by a cast method on a quartz plate and a glass plate, respectively.^c The products were obtained by reprecipitation from CHCl₃/methanol.^d Estimated by GPC calibrated on polystyrene standards.^e The results shown in Ref. 9.^f Shoulder peak.^g Known compound. See Ref. 11.^h Known compound. See Refs. 12,13.

General Methods

NMR spectra were recorded on Bruker AVANCE-400 NMR and AVANCE-600 NMR spectrometers. ¹H- and ¹³C{¹H}-NMR spectra were measured with tetramethylsilane (TMS) as an internal standard. Elemental analysis was carried out with a Perkin–Elmer 2400-CHN instrument. Gel permeation chromatography (GPC) measurements were carried out on a SHIMADZU prominence GPC system equipped with polystyrene gel columns using CHCl₃ as an eluent after calibration with polystyrene standards. MALDI-MS (Matrix Assisted Laser Desorption Ionization Mass Spectrometry) spectra were recorded on AB SCIEX MALDI TOF/TOF 5800. Absorption spectra were recorded using a JASCO V-630 spectrophotometer. The reflection spectra were recorded using a JASCO V-670 spectrophotometer with JASCO ARMN-735 equipment. X-ray diffraction patterns were recorded on a Philip X'Pert MRD with CuK α radiation ($\lambda = 1.542 \text{ \AA}$). Intensity data for crystal structure determination was collected on a Bruker-APEX-II CCD diffractometer with MoK α radiation. Crystals were mounted on MicroMountsTM. A full matrix least-squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters method by SHELXL-97 program. The thicknesses of the films were measured by KOSAKA-ET4000L and Mitsutoyo MDC-25MJ Digimatic Outside Micrometer. Chromaticity diagrams for $L^*a^*b^*$ were measured on a Konica Minolta CM-3600d spectrophotometer with a standard illuminant C and colorimetric observer for applying the CIE-176 Lab color space using a SCI (Specular Component Included) mode[†]. Non-contact surface roughness measurements were carried out on an Olympus

OLS3100 confocal laser scanning microscope. The glossiness of films was determined using a Nippon Denshoku Industries gloss meter VG 7000 at a measurement angle of 60°; the glossiness was scaled based on a reference measurement using black glass (ISO 2813)[‡]. Spectroscopic ellipsometry measurements were carried out on a Woollam M-2000 spectroscopic ellipsometer using a basis-spline (B-spline) function; the incident angle to the samples was adjusted to 70°, 75°, and 80°. Electromagnetic wave shielding effectiveness was characterized with an Agilent Technologies PNA Network Analyzer E8361A using the coaxial line method.

Synthesis

Polymer 1^g: A mixture of Pd₂(dba)₃ (6.9 mg, 7.5 μ mol), P(*t*-Bu)₃HBF₄ (13.1 mg, 45 μ mol), 4-*n*-octylaniline (67 μ L, 0.30 mmol), 4,4'-dibromoazobenzene (101.9 mg, 0.30 mmol), and *t*-BuONa (86.5 mg, 0.90 mmol) was stirred in toluene (1.5 mL) for 24 h at 100°C under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was poured into methanol (200 mL). The precipitate was separated by filtration and washed with methanol, an aqueous solution of ethylenediamine-tetraacetic acid disodium salt, water, and hexane. After reprecipitation from chloroform/methanol, drying *in vacuo* gave a red powder of Polymer 1 in a 94% yield. ¹H-NMR (600 MHz, CDCl₃) δ 7.80 (d, *J* = 8.4 Hz, 4H), 7.20 (d, *J* = 7.8 Hz, 4H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 2.61 (t, *J* = 7.5 Hz, 2H), 1.64 (d, *J* = 6.0 Hz, 2H), 1.42–1.25 (m, 10H), 0.89 (t, *J* = 6.9 Hz, 3H). ¹³C{¹H}-NMR (100 MHz, CDCl₃) δ 149.4, 148.2, 144.0, 140.0, 129.5, 126.2, 123.8, 35.5, 31.8, 31.4, 29.5, 29.4, 29.3, 22.7, 14.1. $M_n = 10,300$, $M_w/M_n = 3.6$.

[†]The measurement was accordance with Standard in development: BS EN ISO 23603:2005(E) (JIS Z 8720) and ISO 11664-4:2008(E) (JIS Z 8781-4): http://www.cie.co.at/Publications/index.php?i_ca_id=477 and http://cie.co.at/index.php?i_ca_id=485.

[‡]The measurement was accordance with Standard in development: BS EN ISO 2813 (JIS Z 8741): <http://standardsdevelopment.bsigroup.com/Home/Project/201001707> and <http://211.67.52.20:8088/xitong/BZ%5C8883252.pdf>.

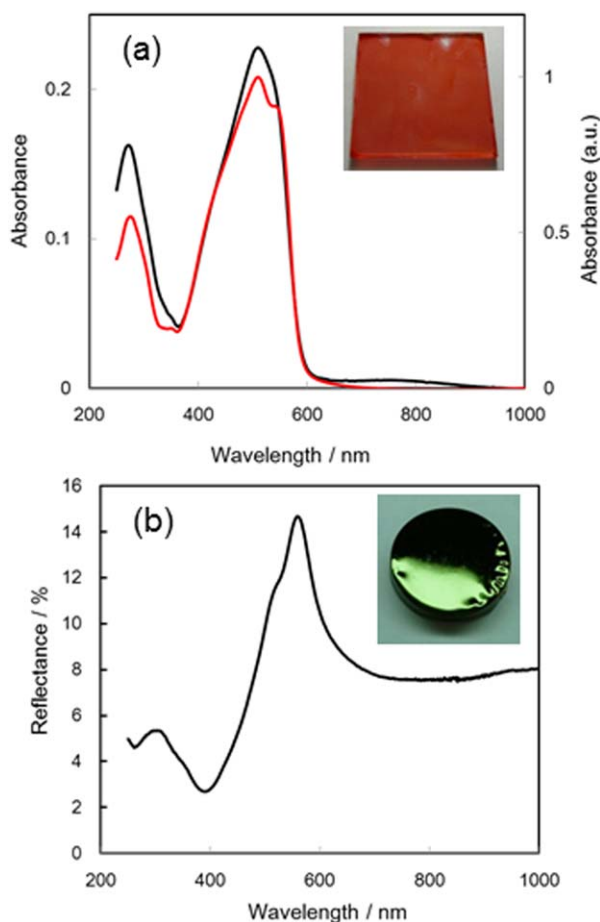


Figure 1. (a) Absorption spectra of Polymer 1 in CHCl_3 solution ($1 \times 10^{-5} \text{ M}$, black) and in thin film state (red), and (b) reflection spectrum of Polymer 1 in thick film state. Insets in (a) and (b) show photographs of the thin and thick films of Polymer 1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Other polycondensation reactions (Scheme 1) were carried out according to the above mentioned procedure. Details of the results and characterization of the polymers and model compounds are summarized in the Supporting Information.

RESULTS AND DISCUSSION

Synthesis and Characterization of Polyaniline Analogs

Polyaniline analog containing azobenzene unit was synthesized by polycondensation of 4-octylaniline with 4,4'-dibromoazobenzene using a Pd-catalyzed C–N coupling reaction⁹; a $\text{Pd}_2(\text{dba})_3$ (dba: dibenzylideneacetone) precatalyst with $\text{P}(t\text{-Bu})_3 \cdot \text{HBF}_4$ in the presence of $t\text{-BuONa}$ gave the corresponding polymer (Polymer 1) in a good yield (Scheme 1). Using the same reaction conditions, polycondensation reactions of four types of aromatic diamine monomers with either 4,4'-dibromoazobenzene or 4,4'-dibromostilbene were conducted (Polymers 2–7). Table I summarizes the results of the polycondensation reactions: The series of polyaniline analogs were obtained in good yields. The molecular weights of the polymers were estimated using gel permeation chromatography (GPC) with chloroform as the eluent. All products are soluble in chloroform, 1,2-dichloroethane, and

tetrahydrofuran. The structures of the polymers were confirmed by ^1H - and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectroscopy. For comparison, model compounds were also prepared using the same method (model 1 and 2).

Photophysical Properties

Thin films and self-supporting films of the polymers were prepared by spin-coating and solvent-casting onto glass plates and/or petri dishes, respectively. Polymers 1–5 are red in solution and in thin films, whereas Polymers 6 and 7 are yellow owing to the presence of the stilbene unit instead of the the azobenzene unit. The UV–vis absorption data for the polymers and model compounds are summarized in Table I. The absorption spectra traces of the polymers in chloroform are similar and their molar absorption coefficients (ϵ) are comparable to those of the model compounds; the absorption is essentially attributed to the chemical structure of the recurring dye units. Alternatively, the introduction of a non-conjugated unit (i.e., $-\text{CH}_2-$ or $-\text{O}-$) into the polymer chain slightly affects the absorbance maxima (λ_{max}): The absorptions of Polymers 4 and 5 are blue shifted by about 10 nm compared with that of Polymer 3, which only has weak π -conjugation along the polymer chain. Because the λ_{max} data of the polymers in chloroform are similar to those in thin film, the interchain interactions such as π – π stacking in the film state must also be negligible; this is likely due to the presence of the bulky triphenylamine unit, which is supported by the results of the X-ray crystallographic analysis of Model 1 (Supporting Information Figure S1).

In contrast to the red color of the thin films, thick films of Polymers 1–5 exhibit green luster. Figure 1 shows the absorption and reflection spectra of Polymer 1 in thin and thick films.

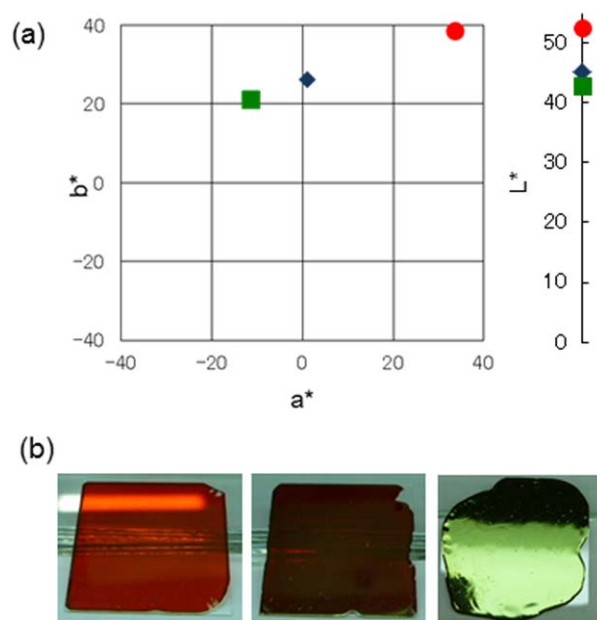


Figure 2. (a) Chromaticity diagram using $L^*a^*b^*$ color system of the films of Polymer 1 with different thicknesses (1 μm (●), 3 μm (◆), and 35 μm (■)). (b) Photographs of the films of Polymer 1 with different thicknesses. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

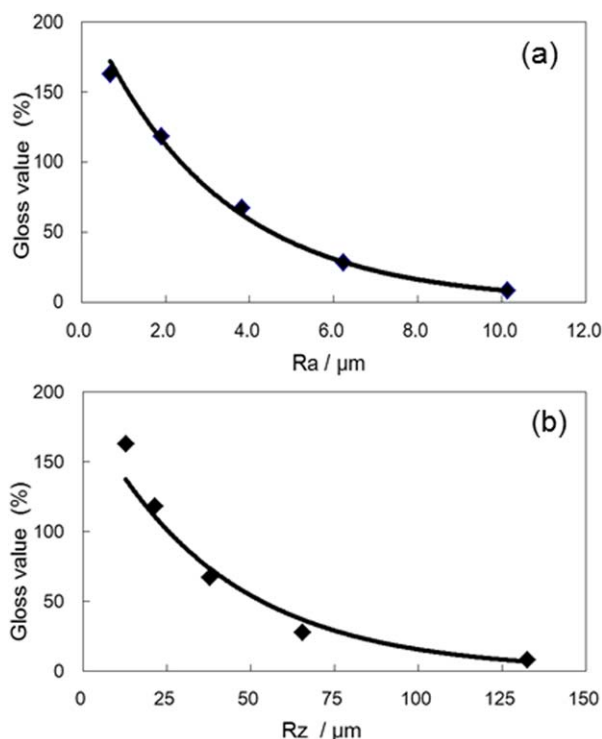


Figure 3. Relationship between glossiness and roughness of the film surface of Polymer 1: (a) arithmetical mean roughness, R_a , and (b) maximum height, R_z .

The absorption and reflection spectra of Polymers 2–7 are shown in Supporting Information Figure S2 and the reflection data are included in Table I. The reflection peaks of the thick films appeared at wavelengths that are about 50 nm longer than those of their absorptions. The non-conjugated polymers (Polymers 4 and 5) exhibit a similar reflective color as Polymer 3, whereas thick films of Polymers 6 and 7 have blue luster. Accordingly, the chemical structure of the dye unit in the polymers is associated with their reflective color; however, π -conjugation along the polymer chains is unlikely.

Elucidation of Reflection

There have been some reports on the metallic lustrous films of π -conjugated polymers consisting of electron-donor and electron-acceptor units^{14–17}; in these films, the metallic luster is assumed to originate from the microstructure of the film, which features π - π stacking interactions, and the reflection spectra were dependent on the incident light angles.¹⁶ In contrast, we observed that the reflection peak position of the Polymer 1 film is independent of the angle of incident light (Supporting Information Figure S3).⁹ In addition, XRD analysis of the film showed a broad diffraction at ~ 4.3 Å (Supporting Information Figure S4), which was indicative of negligible interchain π - π stacking interactions. These features differ from those of the π -conjugated polymer films that show metallic luster; consequently, it is unlikely that the green reflection of Polymer 1 originates from the structural color.^{4–8,18,19}

To evaluate the reflection of polymer films, films of Polymer 1 with different thicknesses were prepared. Figure 2 shows photo-

graphs of the films and their chromaticity diagram using an $L^*a^*b^*$ color system¹²⁰. Films that are more than about 10 μm thick exhibit green luster. This feature is associated with their transparency to visible light: The film with green reflection does not transmit visible light below 600 nm and has low transparency of red light (Supporting Information Figure S5). With respect to the visual color of the thin film of Polymer 1, the chromaticity was also affected by the color of the substrate; when the thin film (about 3 μm thick) was coated onto a black plastic plate, the green reflection was also observed (Supporting Information Figure S6). Therefore, the characteristic red color of the thin film on the glass substrate is attributed to the reflected light from the glass substrate, of which only red transmits through the thin film of Polymer 1.

Because object surface reflection generally consists of diffuse and specular components,^{21,22} we evaluated the dependence of the smoothness of the film surface on the reflection. Films of Polymer 1 with different roughness factors were prepared by casting them onto petri dishes with different roughness. The roughness factor of the film surface and the glossiness were evaluated using a laser scanning confocal microscope and gloss meter, respectively. Figure 3 shows the relationship between the glossiness and roughness of the film surface of Polymer 1: The glossiness decreases with increasing roughness factor of the film

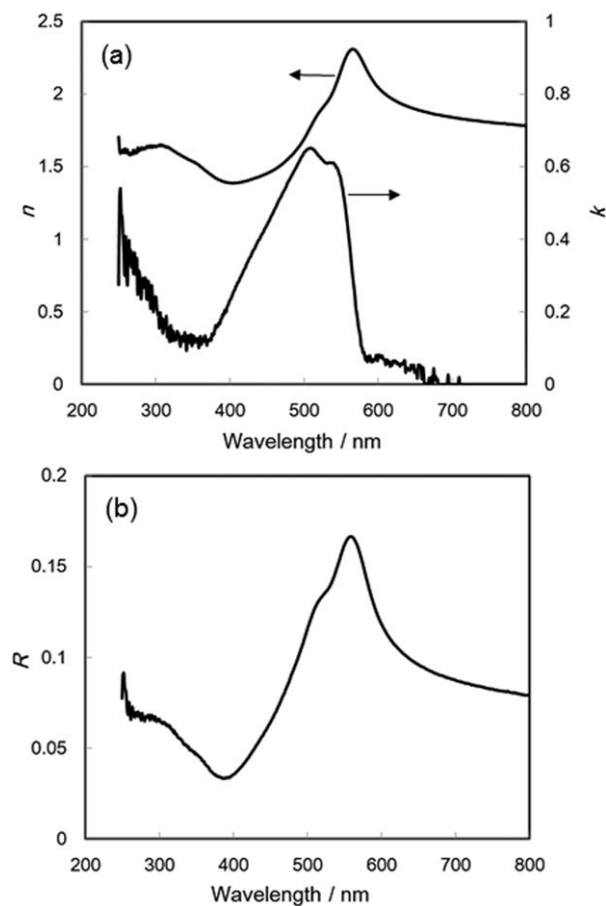


Figure 4. Optical constants of the thick film of Polymer 1: (a) refractive index (n) and extinction coefficient (k) and (b) reflection index (R).

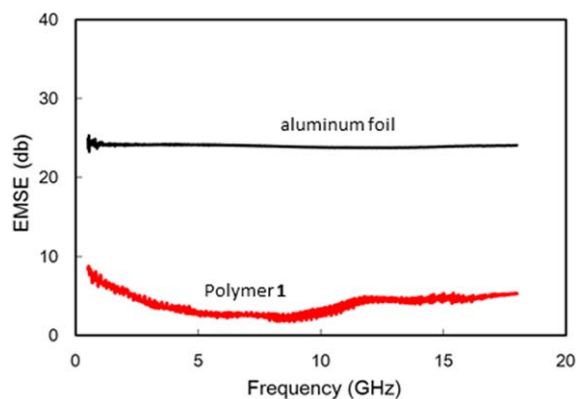


Figure 5. Electromagnetic wave shielding effectiveness of the film of Polymer 1 (100 μm , red) and aluminum foil (11 μm , black). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

surface, revealing that the smoothness of the film surface is an important factor for the reflection.^{18,19}

Spectroscopic ellipsometry is a powerful technique for optical characterization of thin films and bulk materials; it can be used to determine the complex refractive index ($\tilde{n} = n + ik$) as well as the complex dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$).^{23–26} To elucidate the reflection of a polymer film, its optical constants were measured using spectroscopic ellipsometry. Because the thick film of Polymer 1 does not transmit visible light, the ellipsometry data were analyzed using a bulk model to simplify the determination of the relative complex dielectric function; thus, the complex dielectric constant (ε) is described as

$$\varepsilon = (n + ik)^2 = \sin^2 \theta \left[1 + \tan^2 \theta \left(\frac{1 - \rho}{1 + \rho} \right) \right] \quad (1)$$

where θ is the incident angle and ρ is the ratio of the Fresnel reflection coefficients for both p- and s-polarized light ($\rho = r_p / r_s = \tan \Psi e^{i\Delta}$).

The refractive index (n) and extinction coefficient (k) are given by the simple dielectric model as follows:

$$n = \frac{1}{\sqrt{2}} \left[\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2} \right]^{1/2} \quad (2)$$

$$k = \frac{1}{\sqrt{2}} \left[-\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2} \right]^{1/2} \quad (3)$$

Figure 4(a) shows the refractive index and extinction coefficient of the thick film of Polymer 1, as determined from the ellipsometry measurement. Because the extinction coefficient is proportional to the absorption coefficient (i.e., $\alpha = 4\pi k / \lambda$),^{25–29} the extinction coefficient data in Figure 4(a) correlate well with the absorption spectrum of the thin film of Polymer 1 [Figure 1(a)].

The reflection index (R) was determined from n and k : When the complex refractive index (\tilde{n}) of air is 1.0, the reflection index can be tentatively estimated using the following simple equation:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (4)$$

The reflection indices of the thick film of Polymer 1, as determined from the ellipsometry data, are shown in Figure 4(b); the

data correlate well with the reflection spectrum of Polymer 1 [Figure 1(b)]. Similar trends in the reflection indices of Polymers 2–7 were observed via spectroscopic ellipsometry measurements (Supporting Information Figure S7). These results indicate that the optical constants including the refractive index (n) and extinction coefficient (k) of Polymer 1 are closely associated with the green reflection. The response of matter to light is essentially the polarization of the electronic states, and there are numerous vibrational transitions in organic materials.^{25–33} For Polymer 1, the large absorption coefficient at 515 nm is attributed to the π – π^* transition of the diaminoazobenzene recurring unit. Since the oscillator strength is related to the integrated absorption coefficient, the large absorption coefficient and refractive index of Polymer 1 at around 500 nm predominantly dictates the green luster.^{18,19} This is consistent with the green luster of non-conjugated Polymers 4 and 5, whereas the blue luster of Polymers 6 and 7 could be owing to the optical constants of recurring diaminoazobenzene units instead of diaminoazobenzene units.

Transmission of Electromagnetic Wave

Because metals contain large densities of free electrons, electric fields do not penetrate the interior of metal; thus, the metal surface reflects electromagnetic waves.^{27–29,34–36} In contrast, the green reflective film of Polymer 1 should be transparent to electromagnetic waves because it does not contain metals. Figure 5 shows the electromagnetic wave shielding effectiveness of the thick film of Polymer 1; data for an aluminum foil are included for comparison. The attenuation of electromagnetic wave through the film is less than 10 dB across a wide range of frequencies (0.5–18 GHz); therefore, it effectively transmits radio frequency signals. The attenuation is slightly dependent on the film thickness (Supporting Information Figure S8), which is indicative of the lack of free electron carriers. Similar trends in the attenuation of electromagnetic waves were observed for Polymers 2–7.

CONCLUSIONS

Polyaniline analogs containing azobenzene units form green reflective films. Optical characterization of these films confirms that the smoothness of the film surface and the large refractive index and extinction coefficient of the polymers at around 500 nm are crucial to the generation of the green reflection; therefore, the green luster is attributed to the object surface reflection of the dye unit in the polymer film. Although a detailed investigation based on oscillator models is essential for elucidation of the absolute optical properties, this simple protocol reveals the potential for tuning the reflection color of the film through the selection of dye unit. Since these metal-free films could be used for radio-wave transparent materials, they should attract considerable attention for realizing both luxurious finishes and a ubiquitous network. Further studies to expand the range of reflection colors and improve the reflection of the films are currently underway.[§]

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[§]Further optical measurements using multi-angle spectrophotometers will be studied as a next subject.

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