Preparation of Resilient Organic Electrochemical Transistors
Based on Blend Films with Flexible Crosslinkers

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ABSTRACT

Organic electrochemical transistors (OECTs) exhibit high biocompatibility and are expected to be applied in biological sensors. This study focused on crosslinking agents in blend films of a mixed conducting polymer, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), and a thermoresponsive polymer, poly(N-isopropylacrylamide) (PNIPAM), as channel layers to realize reversible temperature response. In addition to the conventional (3-glycidyloxypropyl) trimethoxysilane (GOPS) crosslinker, a poly(ethylene glycol) diglycidyl ether (PEGDE) flexible crosslinker was used to overcome the volume expansion caused by the temperature change. Structural analysis revealed that PNIPAM was segregated on the surface and that the PEGDE crosslinker increased the crystallinity of PEDOT. Blend films with binary crosslinkers (PEGDE and GOPS) exhibited reversible response to temperature cycling. Therefore, the use of a flexible crosslinker in functional blend films can facilitate the fabrication of biosensing OECT devices with higher resilience to the fluctuation of surrounding conditions.
1. Introduction

Organic mixed ionic–electronic conductors are an important class of functional materials in soft electronics and bioelectronic applications.[1-4] These materials transport ions and electrons/holes through hydrophilic ion transport sites and π-conjugated electron/hole transport sites, respectively. The fine-tuning of chemical structures at the molecular level and film structures at the nano- and sub-micrometer levels has been synergistically pursued to achieve high conductivity and coupled transport properties.[5-10] As an application of these materials, organic electrochemical transistors (OECTs) are attracting considerable interest in research that spans fundamental studies of their operation mechanisms to applications.[11-23]. OECTs are three-terminal switching devices similar to organic field-effect transistors (OFETs). Nevertheless, the channel layer of OECT devices is immersed in aqueous electrolyte solutions, injecting ions into the channel layer bulk from the electrolyte, which is different from conventional OFET devices. This unique feature offers biocompatible applications, including in vitro biosignal and biomarker monitoring, body surface monitoring, and implanted modalities.[24-37] For bioelectronic applications, not only the improvement of OECT device performance, but also the functionalization of devices is a critical issue when employing enzymes[25,27,30], ionophores[26,34], and molecularly imprinted membranes.[32,33,37] One method for obtaining functionalized OECT devices is to form multiple layers of channels and functional layers separately by overcoating processes. This method ensures good device performance and stability because the channel has the same layer as conventional OECT devices without functional layers. Compared to the separate functional layer approach, the single-layer approach, based on blend films of mixed conductors and functional materials, is another facile approach for preparing a bioelectronic device with functionalities. In this approach, the most significant concern is to secure the electronic conductive path in the channel region and
the stability of the film under aqueous electrolyte soaking, voltage application, and environmental changes such as temperature and ion strength. Therefore, controlling the phase-separation structure is essential for obtaining stable high-performance OECT devices.

---<<Figure 1>>---

In this paper, we report an approach to satisfy these requirements for functionalized OECT devices based on blend films by tuning the crosslinking agent of the organic mixed conducting materials. In this study, a widely used mixed conductor, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT: PSS, Figure 1), was functionalized with a thermoresponsive polymer, poly(N-isopropylacrylamide) (PNIPAM). PNIPAM has a lower critical solution temperature (LCST) (approximately 32 °C) [38-42] at which coil-globule transition occurs coupled with the dehydration of hydrophilic moieties [43-45]. This transition is beneficial for temperature sensing applications; however, it causes volume expansion and shrinkage. Therefore, the blend film of PNIPAM and mixed conductors should be sufficiently flexible to endure volume changes. This study attempts to overcome this volume change using a flexible crosslinker in film preparation for a proof-of-concept study. To improve the flexibility, a PEG-based crosslinker, poly(ethylene glycol) diglycidyl ether (PEGDE), was used in addition to the conventional rigid crosslinker, (3-glycidoxypropyl) trimethoxysilane (GOPS).[46-48] A PEG-based crosslinker was selected as the new crosslinker because of its flexibility, which has been incorporated into mixed conductors to improve flexibility.[49-51] Some studies have employed PEGDE as a flexible crosslinker for the polymer films of PEDOT: PSS.[52-54] Structural analysis revealed that
PNIPAM was segregated on the surface and that the PEGDE crosslinker increased the crystallinity of PEDOT. The blend film with the binary crosslinker PEGDE+GOPS exhibited a reversible response to temperature cycling. These findings pave the way for the rational design of OECT devices based on blend films.
2. Result and Discussion

The stability of the PNIPAM and PEDOT: PSS blend films was tested using various crosslinker ratios. GOPS and PEGDE were selected as hard and flexible crosslinkers, respectively. All films containing GOPS remained adhered to the substrate even after soaking for two days, whereas the film crosslinked only by PEGDE peeled off from the substrate, while the film shape was maintained (Figure S1). This indicated that only GOPS was responsible for the adhesion to the glass substrate[47,55], and both GOPS and PEGDE contributed to the crosslinking of the polymer materials. The thermal responses of the PNIPAM aqueous solution and the crosslinked PNIPAM film were estimated using differential scanning calorimetry (DSC) measurements (Figure 1 (b)). The results show that endothermic signals are at approximately 33°C for PNIPAM films crosslinked by GOPS, which is close to the critical temperature of PNIPAM in an aqueous solution (32.9 °C). [38-42] This indicates that the crosslinking reaction does not hinder the coil-globule transition of the PNIPAM chains.

Figures 2 (a) and (b) show the UV-vis spectra of the blend films before and after immersion in deionized (DI) water to investigate the crosslinking state inside the blend film. The peaks at approximately 225 nm are attributed to the aromatic rings of PSS, and the broad absorption band in the near-IR region corresponds to the polaron band from the doped PEDOT chains.[56-59] The slight change in these bands upon soaking in DI water indicates that PEDOT: PSS remains
even after immersion in DI water, confirming that PEDOT: PSS is crosslinked by the
crosslinkers. Figures 2 (c) and (d) show the orientation-free spectra of the blend films before and
after immersion in DI water.[60] Note that these spectra were obtained from pMAIRS to
estimate isotropic spectra $A_{\text{iso}}$:

$$A_{\text{iso}} = \frac{1}{3}(2A_{\text{IP}} + A_{\text{OP}}) \quad \text{(equation 1)}$$

where $A_{\text{I.P.}}$ and $A_{\text{O.P.}}$ denote the in-plane and out-of-plane spectra, respectively.[61-63] The peak
at approximately 2970 cm$^{-1}$ is assigned to the CH$_3$ antisymmetric stretching vibration
($\nu_{\text{as,CH}_3}$)[64,65], which is exclusively originated in PNIPAM, and decreases by 18% after DI-
water immersion for blend films with GOPS. This indicates that 82% of PNIPAM remains even
after immersion in DI water. The CH$_2$ symmetric ($\nu_{\text{s,CH}_2}$) and antisymmetric stretching vibrations
($\nu_{\text{as,CH}_2}$) (approximately 2870 and 2930 cm$^{-1}$)[64,65] show larger decreases compared to the
$\nu_{\text{as,CH}_3}$ peaks by 34.0 and 30.1%, respectively. These peaks are derived from both PNIPAM and
PSS, indicating the elution of PSS into DI water, as previously reported.[66-69] However, the as-
cast blend films with PEGDE+GOPS crosslinkers show a larger absorbance of $\nu_{\text{as,CH}_2}$ and $\nu_{\text{s,CH}_2}$
due to the absorption by PEGDE. These peaks decrease on the water soaking (reduced by 67.7
($\nu_{\text{as,CH}_3}$), 74.9 ($\nu_{\text{as,CH}_2}$), and 80.3% ($\nu_{\text{s,CH}_2}$) of as-cast films) due to elution of PEGDE, which is
because of the lack of alkoxy silane (-SiOR) groups that react with hydroxyl groups on substrates
and proceed self-condensation reaction.[70] This was in agreement with the results obtained
from visual observations. The Raman spectra (Figure 2(e)) show a peak at approximately 1430
cm$^{-1}$, which is assigned to the C=C stretch of the PEDOT thiophene rings.[71,72] Although this
peak is sensitive to doping levels and shifts by as much as 40 cm$^{-1}$ upon de-doping [73], the peak
positions of these samples exhibit only a slight shift of less than 3 cm$^{-1}$, indicating that the
doping levels are not significantly changed by blending PNIPAM or using PEGDE crosslinkers. These results indicate that PEGDE acts as a crosslinking agent and has good adhesion properties when used together with GOPS.

The nanostructures of the blend films were evaluated using grazing incidence X-ray diffraction (GIXD) measurements. **Figure 3** (a) and (b) shows the GIXD diffraction patterns of the blend films with GOPS and PEGDE+GOPS crosslinkers. This pattern has a broad halo centered at 6 and 12 nm\(^{-1}\), which is assigned to the lamellar stacking of the PEDOT chains \((h00)\) and PSS amorphous regions, respectively.\[74\text{–}80\] The diffraction observed at approximately 18 nm\(^{-1}\) in the out-of-plane direction correspond to the \((020)\) \(\pi–\pi\) stacking of the crystallized PEDOT (Figure S2).\[74\text{–}80\] The radial integrals from the in-plane \((5^\circ–15^\circ)\) to the out-of-plane \((75^\circ–85^\circ)\) direction of the \(\pi–\pi\) stacking signal are shown in **Figure 3** (c) and (d) to investigate the molecular orientations. The scattering intensity is stronger in the out-of-plane direction, indicating the face-on orientation of the \(\pi–\pi\) stacking of PEDOT chains. The intensity and line width of this region are more significant in the blend film with PEGDE+GOPS crosslinkers than those with the GOPS crosslinker. This indicates that the crystallinity of PEDOT in the films are increased by the binary crosslinker. Note that the weaker diffraction from the lamellar stacking of PEDOT \((h00)\) in PEGDE+GOPS films is in agreement with a previous report on the inverse correlation between the area of this peak and the crystallinity of \(\pi–\pi\) stacking for PEDOT: PSS films with different amount of ethylene glycol addition.\[74\] **Figure 3**e shows the conductivity
and linewidth estimated by fitting the two Gaussian functions. The half-width at half-maximum (HWHM) values of the films with PEDGDE+GOPS crosslinkers is smaller than those of the films with GOPS crosslinkers. This result indicates that PEDGE increases the crystallite size of PEDOT. It is known that polar additives improve the electrical conductivity of PEDOT: PSS films.[66-69] For example, Mengistie et al. showed that adding EG or PEG to PEDOT: PSS solutions led to increased conductivity dependent on the molecular weight or chain length of the additive.[81] The addition of PNIPAM induces a slight change in the HWHM of each crosslinker system, indicating that PNIPAM decreases the crystallinity of PEDOT. The conductivity measured using the four-point probe method correlates with the crystallinity of PEDOT, and the addition of insulating PNIPAM reduces the conductivity. The above results confirm that blending PNIPAM slightly decreases the crystallinity however, the PEGDE crosslinker enhances the crystallinity more significantly than the addition of PNIPAM.

--<<Figure 4>>--

X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) measurements were used to examine the distribution of each component in the depth direction. Figure 4 (a) and (b) shows the depth profiles observed via XPS measurements during Ar⁺ cluster ion etching. Based on the spectral features of the obtained spectra, it was confirmed that this etching condition did not damage the sample surface, as previously reported [82,83]. In the blend films with GOPS and PEGDE+GOPS crosslinkers, the atomic concentration of nitrogen is higher in the surface region than in the bulk film. This result indicates that the structure comprises
segregated PNIPAM on the surface because the nitrogen atoms are contained only in the amide groups of PNIPAM in this system. However, the sulfur content of PEDOT: PSS is lower in the surface region than in the bulk region. This indicates the surface segregation of PNIPAM. Such surface segregation of a lower surface free-energy component is generally driven by the surface energy difference to minimize the interfacial free energy.[84-86] It is thought that the segregated layer in this system is formed by annealing at temperatures above the critical temperature of PNIPAM \( (T_c = 32.9^\circ C) \), where PNIPAM is hydrophobic. For GOPS and PEGDE+GOPS crosslinkers, the thicknesses of the segregated layers are 9 and 6% of the total film thickness, respectively. The smaller percentage of the segregated phase in the blend film with PEGDE+GOPS crosslinkers is due to the high elution of PNIPAM in the PEGDE+GOPS system. This is supported by the fact that PNIPAM dissolves entirely even after the crosslinking reaction using PEGDE and immersion in DI water for two days, whereas the PNIPAM film remains crosslinked with GOPS. **Figures 4** (c) and (d) show the topography images obtained by AFM. These images show mesh-like structures of PNIPAM with RMS roughness of 5.6 and 4.5 nm for blend films with GOPS and PEGDE+GOPS crosslinkers, respectively. It is confirmed that the roughness of neat PEDOT: PSS films (1.6 and 2.0 nm with GOPS and PEGDE+GOPS crosslinkers, respectively) are smaller than that for blend films, supporting the surface-segregated PNIPAM. From these results, it is confirmed that PNIPAM is segregated in a mesh-like structure on the surface.

--<<Figure 5>>--
**Figures 5** (a) and (b) show the cyclic voltammograms of the 1:2 blend films with GOPS and PEGDE+GOPS crosslinkers. Both films show capacitive behavior with the volumetric capacitance $C^*$ of 6.77 and 11.7 F cm$^{-3}$ for films with GOPS and PEGDE+GOPS crosslinkers, respectively. In accordance with previous reports, this capacitive behavior is considered a capacitive process that replaces the holes extracted from the film by metal contact with the injected cations from the electrolyte.[77,87] This capacitive behavior is also observed by impedance spectroscopy, as shown in **Figures 5** (c) and (d). These curves are explained using a two-layer model of the surface-segregated layer of PNIPAM and the bulk layer. The red lines in these panels represent the fitting line of the $R_s-R_1//C_1-R_2//C_2$ circuit, which consists of three components. The impedance spectra of the neat PEDOT: PSS films are explained by a single element, $R_1//C_1$, indicating that the additional $R_2//C_2$ component originates from the PNIPAM-rich phase in the film. Comparing the results of the neat and blend films for GOPS single crosslinkers, the reduction in $C_1^*$ follows a linear relationship with the film composition, reflecting the PEDOT: PSS composition in the bulk layer. This agrees with the behavior of the conductivity, as mentioned above. However, $C_1^*$ values of the films with PEGDE+GOPS crosslinkers are larger than those of the films with GOPS crosslinkers. This is attributed to the increased crystallinity of PEDOT in the bulk layer, as reported in previous experiments[88] and modeling studies. [77] These capacitance results are consistent with the abovementioned GIXD measurements. Based on these results, the composition and crystallinity of PEDOT in the film explain the volumetric capacitance of the blend films.

---<<Figure 6>>---
Figure 6 (a) shows the output and transfer curves of the OECT measurements. These output curves show that the drain current decreases upon applying a positive gate voltage, which is consistent with the depletion-mode operation arising from the dedoping of PEDOT upon the injection of cations from the electrolyte. The transconductance, $g_m$ vs. $V_G$, curves (Figure 6 (b)) show a typical bell shape for OECTs, with a small hysteresis in the gate voltage scan for all compositions in the 1:5 blend. These results indicate that the conduction path through PEDOT in the channel is maintained for all blend ratios tested. For a more detailed analysis, the transconductance per unit volume ($g_m^* = g_m/WLt$, where $W$, $L$, and $t$ are the width, length, and thickness of the channel, respectively) is summarized in Figure 6 (c). The introduction of PEGDE increases $g_m^*$ for the neat and blend films; $g_m^*$ of the neat films increases by approximately four times, which is ascribed to the crystallinity enhancement mentioned above.

Previous studies have reported that the transconductance of OECT devices is proportional to the product of the hole (electron) mobility $\mu$ and capacity for ion injection $C^*$. The deconvolution of electronic mobility and the volume density of bulk charge storage can be done based on the previous measurements; the mobility $\mu$ is related to the conductivity $\sigma$ and carrier density $n$ as $\mu = \sigma/n$. Figure 6 (d) summarizes the parameter $\sigma/\phi$ as an indicator of electronic mobility $\mu$ under an assumption that the doping level of PEDOT is unchanged for all blend ratios. This assumption is justified by the abovementioned Raman and UV-vis spectra. The $\sigma/\phi$ varies over two orders of magnitude, reflecting the conductive PEDOT content in the film, and $\sigma/\phi$ of films with PEDGE+GOPS crosslinkers are higher than that of films with GOPS crosslinkers, reflecting the crystallinity of the film. Using $\sigma/\phi$ and $C^*$ from cyclic voltammetry (CV) measurements (Figure 6 (e)), the indicator of $\mu C^*$ product $\sigma C^*/\phi$ are represented as open
symbols and broken lines in Figure 6 (c). Note that the y-axes of all panels in Figure 6 (c)–(e) span three orders of magnitude. These trends almost follow the obtained $g_m^*$ values, except for the 1:5 blend films. The origin of the deviation at a high PNIPAM content can be attributed to the measurement conditions of conductance, $\sigma$, and OECT device performances performed in dry and wet conditions, respectively. Comparing the change in $\sigma/\varphi$ and $C^*$, it is considered that electronic mobility contributed more than the capacitance for ion injection to the $g_m^*$. In particular, the effect of the PEGDE crosslinkers on the OECT device performance is attributed to the enhancement of crystallinity, which affects the device performance through electronic mobility.

Finally, the devices were tested by temperature cycling across the $T_c$ of PNIPAM to estimate their durability against volume expansion and shrinkage. Figure 7 (a) shows the temperature dependence of the device performance of the blend films with GOPS and PEGDE+GOPS crosslinkers. The device with the blend film crosslinked by GOPS shows an irreversible $g_m$ response to temperature sweep between 20 and 40 °C; the $g_m$ value decreases to 40% of the initial value after the heating process. The microscopic image captured after the temperature cycle (inset of Figure 7a) shows film cracks, indicating that the physical destruction of the conductive path causes an irreversible decrease in $g_m$. In contrast, such an irreversible behavior is not observed for the neat PEDOT: PSS film with the PEGDE+GOPS crosslinker (Figure S3). Based on these observations, it is concluded that the cracks are caused by the volume change of
PNIPAM when the film crosses the critical temperature $T_c$. Note that the decrease in transconductance at the sub-$T_c$ temperature region (20–30 °C) could be related to the shift in the critical temperature by local ionic strength caused by PSS around PNIPAM chains.[89-91] Conversely, the blend film with PEGDE+GOPS crosslinkers show no cracking or delamination and no reversible behavior in $g_m$ during the temperature cycle. The $g_m$ increases upon heating and decreases on cooling, with an average change of 4.0% per 10 °C, whereas neat PEDOT: PSS shows only a small change in $g_m$ (1.1% per 10 °C), as previously reported.[92,93] These results confirm that the reversible temperature response developed using the PEGDE crosslinker is free from irreversible damage to the blend films. Future studies on device optimization and mechanism analysis will pave the way for more prominent temperature responsiveness using OECT devices with thermo-responsive polymers and other biosensor OECT devices with stimulus-responsive polymers.
3. Conclusion

We investigated OECTs based on the blend films of PEDOT: PSS and temperature-responsive polymer PNIPAM. The blend film consisted of a network of PNIPAM segregated on the surface. The flexible crosslinker PEGDE enhanced film stability to prevent crack formation and device degradation during temperature cycling. In addition, crystallinity increased with the addition of PEGDE, which caused an increase in both the conductivity and volumetric capacitance. These findings are expected to contribute to advances in the emerging field of functional OECT devices for biosensors and other applications such as neuromorphic devices.

4. Experiment

PNIPAM polymerization[94,95]

The following compounds were weighed into a polymerization tube: 2.07 g (18.3 mmol) of NIPAM (Tokyo Kasei I0401), 0.0105 g (0.0640 mmol) of AIBN recrystallized twice with methanol (molar ratio to monomer:3.50 × 10⁻³), and 15 mL of anhydrous methanol (Wako Pure Chemicals). The tubes were then frozen and degassed thrice under vacuum. An overnight polymerization reaction was then initiated by placing the polymerization tube in an oil bath at 60 °C. After overnight polymerization, the polymer was transferred to an egg-shaped flask, and the solvent was removed using an evaporator. The polymer was dissolved in acetone, which was then removed using an evaporator, and the polymer was vacuum-dried. The polymer was then re-precipitated using acetone and hexane as the solvents. The process was repeated thrice for overnight vacuum drying to remove the monomers. The polymer was then purified by dialysis.
using a cellulose tube (fractional molecular weight of approximately 12,000–14,000, pore size of 5 nm). The molecular weight of this polymer was estimated to be $M_w = 3.3 \times 10^4$, and $M_w/M_n$ was determined to be 1.6 by SEC measurements using polystyrene standards. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 0.9–1.2, 1.3–2.4, 3.8–4.2, 5.6–7.2$ ppm.

**Film Preparation**

The PEDOT: PSS solution was prepared as reported.[19,23,34] PEDOT: PSS (Clevios, pH 1000) and EG (FUJIFILM Wako Pure Chemical Co.) were used as polar solvents, DBSA (Tokyo Kasei) was used as the surfactant, and the mixture was sonicated for 15 min. The premixed mother solution was mixed with the PNIPAM aqueous solution at different weight ratios (PEDOT/PSS: PNIPAM = neat, 1:1, 1:2, and 1:5). Crosslinkers GOPS and PEGDE in different molar ratios (GOPS: PEGDE = 10:0, 8:2, 6:4, 4:6, 2:8, and 0:10) were added to the solution while maintaining the total volume ratio at 1%. The final solution was then sonicated for 15 min, spin-coated at 1000 rpm onto substrates, and annealed at 130 °C for 30 min to obtain a spin-coated film. Each substrate was cleaned in an ultrasonic bath with acetone, isopropyl alcohol, and DI water, and treated with UV-ozone for 30 min before use. The obtained films were immersed overnight in DI water.

**Spectroscopic Analysis**

Thin films were prepared on quartz substrates using the procedure described above. UV-vis measurements were performed using a spectrometer (V-670; JASCO). For infrared multiple-angle incidence resolution spectrometry (IR-MAIRS) and XPS measurements, thin films were prepared on Si wafers using the procedure described above. IR-MAIRS measurements were performed using a spectrometer (iS-50; Thermo Fisher Scientific) equipped with a sample
rotation stage in dry air. The XPS measurements were performed at the Nara Institute of Science and Technology using an XPS instrument (PHI5000VersaProbe II, ULVAC PHI). The measurements were conducted using a monochromatized AlKα x-ray source with an incident angle of 90° and an emission angle of 45°. The sputtering conditions were 10 kV and 20 nA for 10 min. The measurements were performed while drilling the film surface with Ar-cluster ions.

**GIXD measurement**

Thin films were prepared on Si wafers using the aforementioned procedure. GIXD measurements were performed using monochromated synchrotron radiation at the BL46XU beamline at SPring-8, with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2021B1953). The X-ray wavelength and incident angle were 0.1 nm and 0.12°, respectively. All measurements were performed under ambient atmosphere.

**Conductivity measurement**

Thin films were prepared on glass substrates by using the aforementioned procedure. The measurements were performed using the four-point probe method with a resistance meter (HIOKI 3541) connected to a four-point probe at the probe-to-probe distance of 5 mm (Loresta LSP; Mitsubishi Chemical Analytech).

**Electrochemical measurement**

Electrochemical measurements were performed by depositing the blend film on an indium-tin oxide (ITO) substrate. For electrochemical impedance spectroscopy (EIS) measurements, an LCR meter (ZM2376, NF Corp.) was used at a frequency range of 100 mHz–100 kHz and sine-wave AC voltage amplitude of 0.01 Vrms. PBS (0.0027 M KCl, 0.137 M NaCl) was used as the
electrolyte with Ag/AgCl as the counter electrode and ITO as the working electrode. CV measurements were performed on a potentiostat analyzer (ECstat-301; EC Frontier Co., Ltd.) using the three-electrode method. PBS (0.01 M) was used as an electrolyte, with Ag/AgCl as the reference electrode, and a Pt wire as a counter electrode; sweep rates were 20, 30, 50, 100, and 200 mV s⁻¹.

**OECT fabrication and measurement**

OECT substrates were prepared by depositing 10 nm Ti and 100 nm Au on glass substrates that had been pre-cleaned using the method described above. The substrate was spin coated with SU-8 3005 and patterned in the channel region using a mask aligner (MA-10B, Mikasa). The self-assembled monolayer (SAM) treatment on electrodes was performed by immersing the substrate overnight in 0.5 mM α-thioglycerol (TG) (Tokyo Kasei) in dehydrated ethanol (FUJIFILM Wako Pure Chemical Co.) solution to deposit the SAM layer on the Au electrode.[96] The fabricated OECT devices (channel length $l = \sim 300 \mu$m, channel width $w = \sim 1.0$ mm) were analyzed using a semiconductor parameter analyzer (4155C; Keysight). The measurements were performed in a Faraday cage with a temperature-controlled stage, using PBS (0.01 M) as the electrolyte. The temperature of the device was controlled using a Peltier stage (HMC-11W-0100; Hayashi Repic) and monitored using a thermocouple immersed in an electrolyte solution.
FIGURES

Figure 1. (a) Synthetic scheme of PNIPAM, (b) DSC curves of PNIPAM aqueous solution (black, broken line), PNIPAM film crosslinked by GOPS (black, solid line), and blend films of PEDOT:PSS and PNIPAM crosslinked by GOPS (red 1:2, blue 1:5). (c-e) Chemical structures of GOPS, PEGDE, and PEDOT:PSS.
Figure 2. Spectroscopic analysis of the blend films (black) before and (red) after immersion into water: (a,b) UV-vis and (c,d) IR-MAIRS spectra of 1:2 blend films crosslinked with (a,c) GOPS and (b,d) PEGDE+GOPS (8:2).
Figure 3. GIXD analysis of blend films: (a,b) GIXD patterns of 1:1 blend films crosslinked with (a) GOPS and (b) PEGDE+GOPS. (c,d) Radial integration of intensity from 5 to 85° for (a) and (b). (e) Plot of linewidth at approximately 18 nm⁻¹ and conductivity of films (circles: PEDOT:PSS, triangles: PEDOT:PSS+PNIPAM (1:1), open symbols: PEGDE+GOPS (8:2) crosslinker, closed symbols: GOPS crosslinker)
Figure 4. Topographic analysis of blend films: (a,b) XPS depth profiles and (c,d) AFM images of 1:2 blend films crosslinked with (a,c) GOPS and (b,d) PEGDE+GOPS (8:2).
Figure 5. Electrochemical analysis of blend films: (a,b) cyclic voltammograms and (c,d) impedance spectra of 1:2 blend films crosslinked with (a,c) GOPS and (b,d) PEGDE+GOPS. (a,b) Cyclic voltammograms measured at 30, 50, 100, and 200 mV s$^{-1}$. (c,d) Red solid and broken lines show fitting lines by an equivalent circuit shown as the inset.
Figure 6. OECT device analysis of blend films: (a) output and (b) transfer curves of 1:2 blend films crosslinked with PEGDE+GOPS. (c,d,e) Transconductance $g_m$, conductivity $\sigma$ normalized by film composition $\phi$, and capacitance $C^*$ plotted against the PEDOT:PSS content in blend films $\phi$. Open symbols and broken lines indicate the product of each parameter.
Figure 7. Temperature response of OECT devices: (a,b) Dependence of transconductance on the temperature of the electrolyte 1:2 blend films crosslinked with GOPS (black) and PEGDE+GOPS (red). Panel (b) shows enlarged curve for PEGDE+GOPS. Inset of (a) shows a photograph of blend film crosslinked with GOPS on gold electrode after temperature cycling (scale bar: 100 μm).
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1433.


SUPPORTING INFORMATION

Stability of the blend films PNIPAM/PEDOT:PSS

Figure S1. Optical images of spincoated PEDOT:PSS films crosslinked by GOPS:PEGDE = 10:0, 8:2, 6:4, 4:6, 2:8, 0:10 mixtures.
GIXD patterns of PEDOT:PSS and blend films

**Figure S2.** In-plane and out-of-plane GIXD patterns for each film.
Temperature response of OECT device based on neat PEDOT:PSS film

**Figure S3.** Temperature response of a neat PEDOT:PSS OECT device crosslinked with PEGDE+GOPS.