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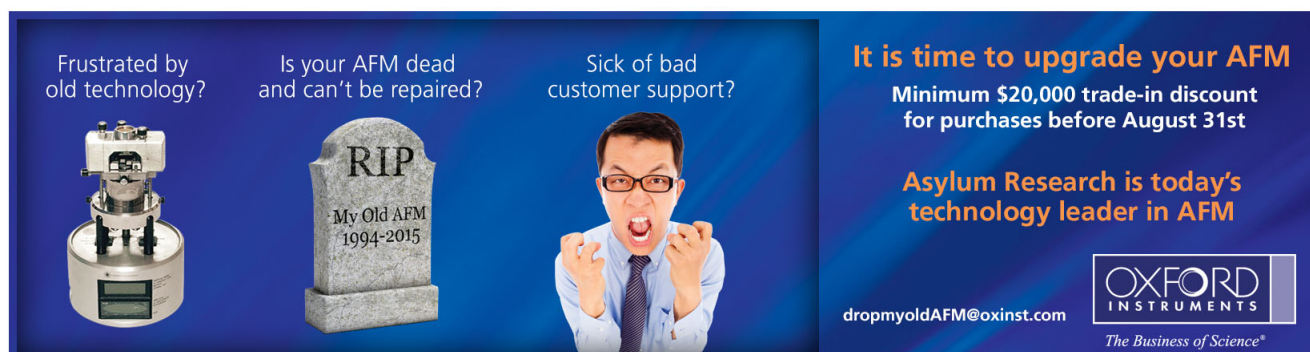
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Effect of incorporation of ethylene glycol into PEDOT:PSS on electron phonon coupling and conductivity

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The effect of incorporation of ethylene glycol (EG) into poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) on electron phonon coupling and conductivity is investigated. It is shown that the carrier density (N_C) increases significantly and the carrier mobility (μ) increases slightly at 300 K. The increased intensity of the Raman spectrum between 1400 and 1450 cm^{-1} , following EG treatment (that is, the quinoid-dominated structures of the PEDOT chain), leads to an increase in the number of polarons (bipolarons), which leads to an increase in N_C . In addition, μ in PEDOT:PSS samples with or without EG addition exhibits a strong temperature dependence, which demonstrates the dominance of tunneling (hopping) at low (high) temperatures. The high conductivity of PEDOT:PSS samples with the addition of EG is attributed to the combined effect of the modification of the electron-phonon coupling and the increase in N_C (μ). © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4921930>]

I. INTRODUCTION

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is the most studied conducting polymer system, because it is an important hole-transporting layer in organic light-emitting diodes and organic photovoltaics. PEDOT:PSS represents the next-generation of electrodes because of its high transparency in the visible range, its solution processability, its high work function, and its significant mechanical flexibility.^{1–14} With the widespread use of PEDOT:PSS, a number of studies are attempting to determine and improve its properties. A common method that is used to improve the properties of PEDOT:PSS is a chemical treatment that involves the addition of co-solvents, which results in considerable improvement to the polymer's conductivity.^{1,13–17} However, PEDOT:PSS exhibits strong electron-phonon coupling,^{18,19} which results in the low carrier mobility at room temperature.²⁰ While the electron-phonon coupling in inorganic semiconductors is rather weak, in their narrow-band organic counterparts it plays a prominent role. In order to achieve high conductivity in PEDOT:PSS, the electron-phonon coupling must be modified. The incorporation of ethylene glycol (EG) into PEDOT:PSS makes it possible to decouple electrons and phonons. Treatment of PEDOT:PSS films with EG to control conductivity has been reported.^{1,17,21–25} EG has been shown to significantly enhance the electrical properties of PEDOT:PSS in comparison with other solvents.¹ Kim *et al.* obtained conductivities as high as 735 S/cm for PEDOT:PSS (PH 1000 from H. C. Starck) with the addition of EG and demonstrated a solvent post-treatment method which remarkably increases the conductivity up to 1418 S/cm.¹⁷ Mengistie *et al.* suggested that the increase in electrical conductivity, especially through selective removal of PSS, is a key strategy in increasing the thermoelectric

performance of PEDOT:PSS.²³ However, conductivity is a product of both the density of the carriers (N_C) and their mobility (μ), and it is still unclear how much each of these components contributes to an increase in conductivity. While it is clear that incorporating EG into PEDOT:PSS improves device performance, further experimental work is necessary to understand the underlying mechanism(s). In this study, the effect of the incorporation of EG on the electrical properties of the PEDOT:PSS film is determined. N_C increases significantly and μ increases slightly at 300 K. It is found that the addition of EG leads to a change in the chemical structure of PEDOT:PSS that increases the number of polarons (bipolarons) and increases N_C . The temperature-dependent carrier mobility for PEDOT:PSS films also exhibits a hopping-to-band transition. Depending on the electron-phonon coupling strength, the charge transport mechanism is classed into the polaron model. The results indicate that the increased μ in PEDOT:PSS due to the incorporation of EG is attributed to a modification of the electron-phonon coupling.

II. EXPERIMENTAL DETAILS

PEDOT:PSS (Clevios PH1000) was purchased from Heraeus. The water dispersion containing 1.3 wt. % of PEDOT:PSS and the water dispersion with the additional solvent of EG (1.0, 3.0, and 5.0 wt. %) were, respectively, deposited on glass substrates by spin coating [referred to as PEDOT:PSS:EG(I), PEDOT:PSS:EG(II), and PEDOT:PSS:EG(III)]. The glass samples were cleaned in chemical cleaning solutions of acetone and methanol, rinsed with de-ionized water and blow-dried with N_2 . Spin casting was performed at 500 rpm for 5 s and at 1500 rpm for 30 s for each cast layer. After deposition by spin coating, the films were baked at 150 °C for 30 min on a hotplate. The procedures from coating to drying were repeated 5 times to prepare a thicker layer. The thickness of the PEDOT:PSS

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(PEDOT:PSS:EG) film, as estimated using an ellipsometer, was 100 nm. The effect of the incorporation of EG on the structural properties of PEDOT:PSS films was examined using Raman spectroscopy. A 532-nm laser was used for excitation. The surface morphology of PEDOT:PSS (PEDOT:PSS:EG) was studied using atomic force microscopy (AFM). The values for N_C , μ , and resistivity (R_r) are obtained from the Hall measurements (Ecopia HMS-5000) in the van der Pauw configuration. The electrodes were fabricated by depositing Au metal onto the PEDOT:PSS (PEDOT:PSS:EG) layer through a shadow mask. The HMS-5000 includes software with a current-voltage curve that is capable of checking the ohmic integrity of the user-made sample contacts.

III. RESULTS AND DISCUSSION

In order to obtain R_r (N_C and μ) as a function of temperature (T), the Van der Pauw–Hall measurements were performed in the temperature range, 110–320 K. The PEDOT:PSS films with and without EG addition demonstrate p-type behavior. Figure 1 shows the temperature-dependent R_r for PEDOT:PSS (PEDOT:PSS:EG) films. Increased conductivity is achieved by incorporating EG into PEDOT:PSS. The resistivity of PEDOT:PSS depends on humidity, and EG has a high affinity for water. Lower humidity results in lower resistivity. However, the electrical conductivity increases as the EG content ([EG]) increases, reaching a maximum at [EG] = 3.0 wt. %, and then decreasing as [EG] increases beyond that point. An excessive concentration of EG can increase the distance between the polymer chains or the crystallites, which increases the resistivity of the composite. Clearly, a suitable value for [EG] is necessary.

Figure 2 shows the temperature-dependent N_C for PEDOT:PSS (PEDOT:PSS:EG) films. The derived values for N_C are consistent with the reported values of Wei *et al.*²⁴ Figure 3 shows the temperature-dependent μ for PEDOT:PSS (PEDOT:PSS:EG) films. In agreement with a previously reported result,²⁴ it is found that the derived values of μ vary in the range, 0.05–0.60 cm² V⁻¹ s⁻¹. In addition, N_C increases significantly and μ increases slightly at 300 K. It is

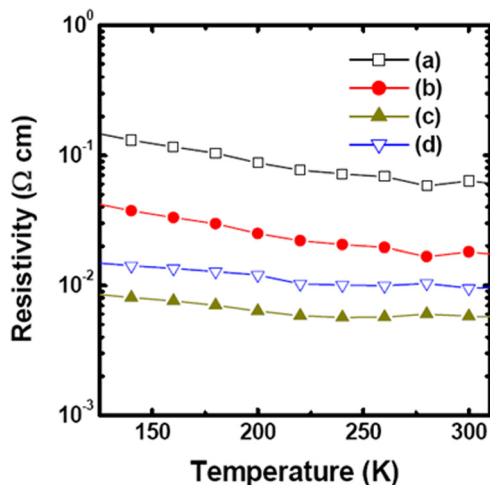


FIG. 1. Resistivity as a function of temperature [(a) PEDOT:PSS, (b) PEDOT:PSS:EG(I), (c) PEDOT:PSS:EG(II), and (d) PEDOT:PSS:EG(III)].

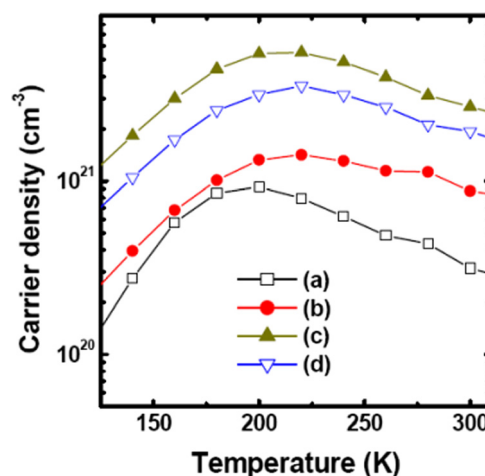


FIG. 2. The carrier concentration as a function of temperature [(a) PEDOT:PSS, (b) PEDOT:PSS:EG(I), (c) PEDOT:PSS:EG(II), and (d) PEDOT:PSS:EG(III)].

suggested that the incorporation of EG results in the removal of the insulating PSS component from PEDOT:PSS films,^{17,23} which causes an increase in N_C . The addition of EG allows the PSS chains to reorganize and the PEDOT nanocrystals to pack together to form a layered structure with a higher order.²⁴ This ordering effect increases the number of polarons (bipolarons), which increases N_C for the PEDOT:PSS films.^{24,26} This effect is linked to the increased number of polarons (bipolarons) and is associated with transitions between quinoid- and benzoid-dominated structures.²⁷ The PEDOT chain stores charge in the form of polarons/bipolarons; both polarons and bipolarons can propagate an electrical current along the polymer chain.^{25,28,29} The effect of ultraviolet (UV) irradiation on the electrical property of PEDOT:PSS films was also determined.⁶ It is found that μ increases and N_C does not change significantly.⁶ The increased electrical conductivity is mainly the result of an increase in μ .⁶ It is deduced that water molecules mostly influence N_C and UV treatment significantly affects changes in μ .

In order to understand the origin of an increase in μ , an analysis using the temperature-dependent Hall-effect

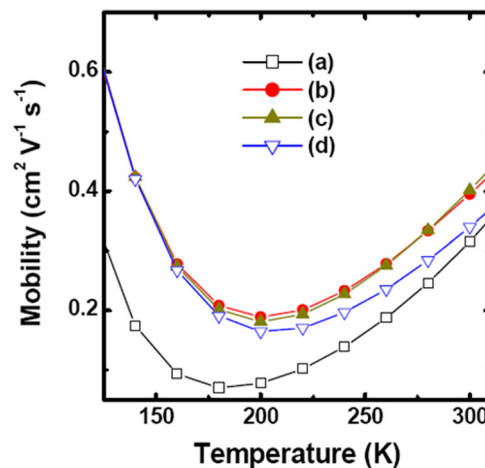


FIG. 3. The carrier mobility as a function of temperature [(a) PEDOT:PSS, (b) PEDOT:PSS:EG(I), (c) PEDOT:PSS:EG(II), and (d) PEDOT:PSS:EG(III)].

characteristics is presented. μ is increased from 0.3 to $0.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ by incorporating EG at room temperature. In addition, μ in PEDOT:PSS films exhibits unexpectedly strong temperature dependence (Fig. 3), which demonstrates that tunneling (hopping) is dominant at low (high) temperatures.³⁰ According to polaron models, the total mobility is expressed to a good approximation as the sum of two contributions³⁰

$$\mu = \mu_{\text{tun}} + \mu_{\text{hop}}, \quad (1)$$

$$\mu_{\text{tun}} = \frac{qa_s^2\omega_o}{k_B T} \left[\frac{g^2}{\pi \sinh\left(\frac{\hbar\omega_o}{2k_B T}\right)} \right]^{0.5} \exp\left[\frac{-2g^2}{\sinh\left(\frac{\hbar\omega_o}{2k_B T}\right)} \right], \quad (2)$$

$$\mu_{\text{hop}} = \frac{qa_s^2 t_i^2}{k_B T \hbar^2 \omega_o} \left[\frac{\pi \sinh\left(\frac{\hbar\omega_o}{2k_B T}\right)}{g^2} \right]^{0.5} \exp\left[-2g^2 \tanh\left(\frac{\hbar\omega_o}{4k_B T}\right) \right], \quad (3)$$

where μ_{tun} is the tunneling mobility, μ_{hop} is the hopping mobility, g is the electron-phonon coupling constant, q is the elementary charge, a_s is the spacing between molecules, \hbar is $h/2\pi$ (h is the Planck constant), $\hbar\omega_o$ is the phonon energy, t_i is the transfer integral, and k_B is Boltzmann's constant. Using the experimental data, the charge-transport parameters are derived from the equations using the nonlinear least-squares method and compared, as demonstrated in Table I. It is found that the value of a_s is not affected by EG treatment. However, the values of $\hbar\omega_o$, g , and t_i are significantly affected by EG treatment. The contribution to the polaron binding energy that arises from the external (lattice) degrees of freedom is considered. Coropceanu *et al.* found that non-local couplings increase the polaron binding energy (E_{pol} , $E_{\text{pol}} = \hbar\omega_o g^2$) and increase the bandwidth.³⁰ Interestingly, the incorporation of EG into PEDOT:PSS leads to a reduction in g , a weakening of the local electron-phonon coupling, and a reduction in the values of E_{pol} and t_i . The local electron-phonon coupling plays a key role in the charge transport in PEDOT:PSS. In the organic material, the strong electron-phonon interaction causes lattice distortion around the electron, which moves along the chain but is also trapped by the polarized field that is formed.³¹ It is reasonable to conclude that the increased μ in PEDOT:PSS due to the incorporation of EG is associated with the modification of electron-phonon coupling.

The addition of EG can cause structural reorganization in PEDOT nanocrystals, which can be evaluated by Raman spectrum studies. Figure 4 shows the Raman spectra for PEDOT:PSS films with and without EG addition. The

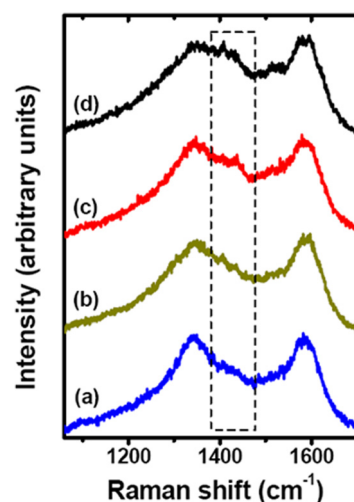


FIG. 4. Raman spectra [(a) PEDOT:PSS, (b) PEDOT:PSS:EG(I), (c) PEDOT:PSS:EG(II), and (d) PEDOT:PSS:EG(III)].

polymeric structure is affected by incorporating EG. Between 1200 and 1400 cm^{-1} , peaks are assigned to C–C stretch vibrations, and between 1400 and 1600 cm^{-1} to C=C stretch vibrations, which renders them particularly sensitive to the presence and the degree of (de-)localization of holes.²⁷ It is found that the intensity of the band between 1400 and 1450 cm^{-1} increases following EG treatment. This effect is linked to the increased number of polarons (bipolarons) and is associated with transitions between quinoid- and benzoid-dominated structures. A polaron corresponds to a positive charge on a unit and a bipolaron corresponds to two positive charges that are delocalized over several units.^{25,26} The benzoid structure may be the favorite structure for a coil conformation and the quinoid structure may be the favorite structure for a linear or expanded-coil structure.²⁶ Transition from polarons to bipolarons is due to the conformational change from a coil to a linear or expanded-coil structure, so the charge becomes more delocalized on the PEDOT chains.²⁶ Bipolarons can move two orders of magnitude faster than polarons in conducting polymers,^{25,29,32} so the increase in the electrical conductivity of PEDOT:PSS samples with EG addition can be explained in terms of the increased number of polarons (bipolarons). The enhanced intensity of the band between 1400 and 1450 cm^{-1} following EG treatment (Fig. 4) demonstrates that the quinoid-dominated structures of the PEDOT chain serve to increase the number of polarons (bipolarons), which results in an increase in N_C .^{26,33} Maeng *et al.* found that the charge traps in PEDOT:PSS affect electronic conduction through the PEDOT:PSS/ZnO nanowall network device.³ It is suggested that the coil conformation turns into a linear or expanded-coil conformation and that the number of the charge-trapping-related defects is reduced after EG treatment, which increases the electrical conductivity of PEDOT:PSS films. It is also suggested that the incorporation of EG leads to changes in the chemical structure of PEDOT:PSS, which weaken the local electron-phonon coupling and result in an increase in the values of N_C and μ .

In order to obtain a greater understanding of the increase in conductivity and to determine the possible changes in the

TABLE I. Fitting parameters and results.

	g^2	$\hbar\omega_o$ (meV)	a_s (nm)	t_i (eV)
PEDOT:PSS	6.40	55	0.7	0.62
PEDOT:PSS:EG(I)	5.00	60	0.7	0.40
PEDOT:PSS:EG(II)	5.20	61	0.7	0.47
PEDOT:PSS:EG(III)	5.15	61	0.7	0.42

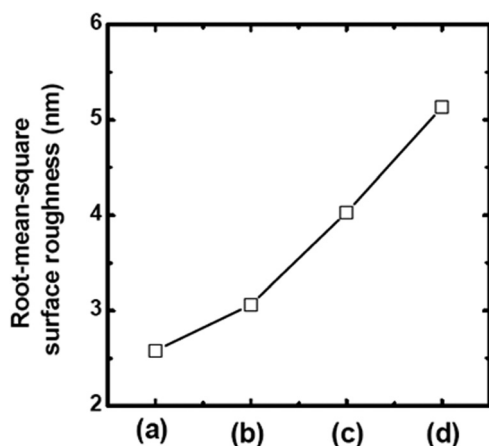


FIG. 5. The root-mean-square surface roughness [(a) PEDOT:PSS, (b) PEDOT:PSS:EG(I), (c) PEDOT:PSS:EG(II), and (d) PEDOT:PSS:EG(III)].

morphology and the correlation between morphology and performance, AFM images were obtained. Figure 5 shows the root-mean-square surface roughness (R_{rms}) of PEDOT:PSS films as a function of [EG]. It is found that the value of R_{rms} increases as [EG] increases. This explains why the electrical conductivity of PEDOT:PSS:EG(III) is lower than that of PEDOT:PSS:EG(II). As the R_{rms} value increases significantly, the total number of particle boundaries within a given volume or area increases and there are many energy barriers for charge conduction. The energy barrier for inter-chain and inter domain charge hopping increases, which results in inferior charge transfer between the PEDOT chains. Mengistie *et al.* suggested that conductivity is related to film morphology.²² It is suggested that an appropriate [EG] value is necessary.

IV. CONCLUSIONS

It is shown that the simple addition of a suitable wt. % of EG in PEDOT:PSS can significantly increase the electrical conductivity. Although numerous studies have been published on the optimization of the process conditions that are necessary to improve the electrical conductivity of PEDOT:PSS, the underlying mechanisms are still not clear. This study shows that N_C increases significantly and μ increases slightly at 300 K. In order to understand this phenomenon, an analysis using the temperature-dependent Hall-effect characteristics is presented. A crossover from a band-like charge transport to a hopping motion is observed for PEDOT:PSS (PEDOT:PSS:EG) films. In order to obtain a greater understanding of the increase in conductivity, the Raman spectroscopy measurement is performed. An increased intensity is observed for the band between 1400 and 1450 cm^{-1} following EG treatment [that is, the quinoid-dominated structures of the PEDOT chain that serve to increase the number of polarons (bipolarons)]. The results demonstrate that the addition of EG affects the electrical conductivity of PEDOT:PSS by increasing N_C (μ) and by modifying the electron-phonon coupling. This understanding allows further development of PEDOT:PSS films with even greater conductivity and for the development of highly efficient optoelectronic and electronic devices.

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