

# Development of Anchored Oligothiophenes on Substrates for the Application to the Tunable Transparent Conductive Films

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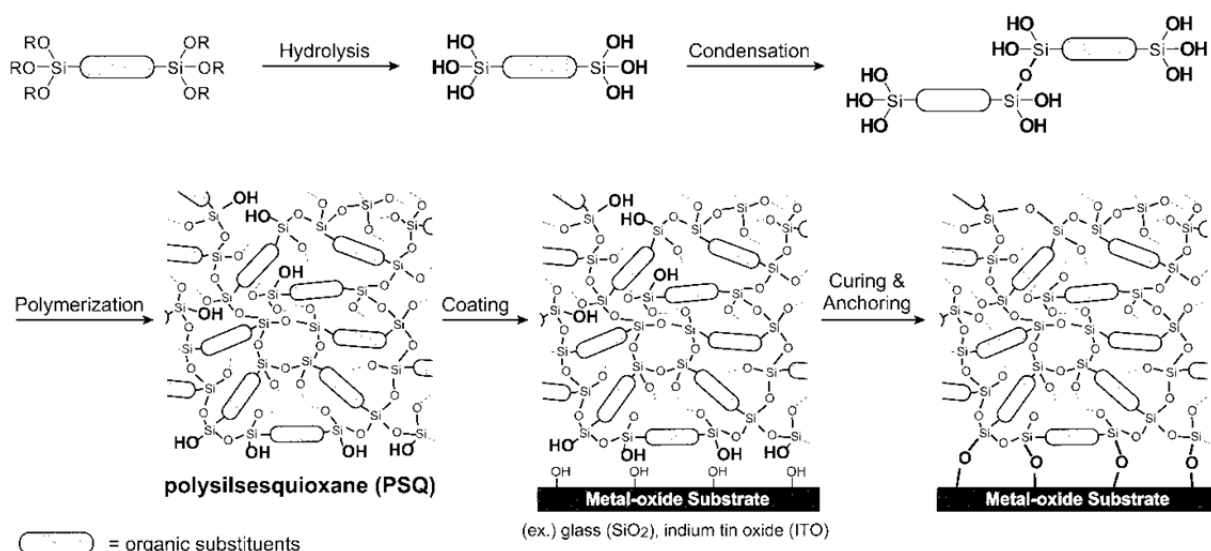
## **Abstract**

Bis(triethoxysilyl)-substituted oligothiophene with a moderate  $\pi$ -conjugation length was newly synthesized and polymerized to give a polysilsesquioxane network having oligothiophene units dispersed homogeneously without phase separation. The polymer was fixed on glass or ITO substrate by spin-coating and annealing. The resulting film exhibited a high mechanical strength due to the covalent bonding with the substrates, and was electrochemically stable even after 300 redox cycles in electrolyte solution. Chemical oxidation of the polymer films yielded electrically conductive and almost transparent films.

*Keywords:* Oligothiophenes; Polysilsesquioxanes; Anchoring; Conducting Materials

## **1. Introduction**

Organic-inorganic hybrid materials are opening a new field of materials science because of a wide range of applications. Among them, the hybrid materials based on siloxane-network are very attractive due to the excellent feature of siloxane bond [1] and thus many reports have been done. From the viewpoints of synthetic approach and the resulting materials structure, siloxane-based hybrid materials can be divided into two general classes [2]. Class I corresponds to the nanocomposite materials, which are synthesized by the inorganic hydrolytic polycondensation (sol-gel reaction) of tetraalkoxysilane monomer incorporated with low molecular weight organic compounds as the dopants. In this class of hybrid materials, the organic dopants are just embedded in the inorganic matrix, and are likely to be isolated due to phase separation. Class II corresponds to the nanostructured hybrid materials prepared from the sol-gel reaction using trialkoxysilane-based precursor monomers having organic substituents, and the resulting network polymers are called as polysilsesquioxanes (PSQs). In the case of PSQs, the introduced organic substituents are covalently linked to the siloxane network, so that the phase separation between the organic substituents and polymer network can be suppressed and organic substituents are strongly fixed in the network. Furthermore, when the PSQs are coated on the metal-oxide substrates, terminal silanol groups of PSQs will react with hydroxy groups on the surface of metal-oxide substrates such as glass and ITO (Scheme 1). Thus, the organic groups in PSQs can be also fixed on the substrates through the siloxane polymer network. From this advantage, novel high-performance materials based on PSQs are applied to surface modification such as the water repellent coating for automobiles, catalyst supports, adsorbents, optics, and biosensors [3].



**Scheme 1.** Formation of polysilsesquioxanes by the hydrolysis and condensation of trialkoxysilyl-substituted monomers and their anchoring onto metal-oxide substrate.

We demonstrate here the new application of PSQs to transparent and conductive films with the tunability of electrical properties. As transparent and conductive films, commercially available poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT-PSS) has been widely used in the charge-injection layer in organic electroluminescence displays and the charge-collecting layer in the organic thin-film solar cells, but there are some problems on its mechanical strength and solubility [4]. Wrighton et al. and Wu et al. independently reported the preparation of monolayer of silane-bearing pyrrole on metal-oxide surfaces using trialkoxysilyl-substituted pyrrole, and the electrochemical or chemical deposition of poly(pyrrole)s on it [5]. However, their techniques cannot control the degree of polymerization, and thus the electronic natures of the formed films cannot be controlled.

In this communication, our idea is realized by introducing oligothiophenes with well-defined structures as electrically conductive units in PSQs. Oligothiophenes are well-studied as a series of photo- and electroactive materials, and show electrical conductivities by chemical and/or electrochemical oxidation (p-doping) [6]. Also, their conductive and energetic properties can be easily controlled by changing their  $\pi$ -conjugation

length and by introducing electron donating or withdrawing groups on the  $\pi$ -conjugated chains. These natures can lead to the desirable tuning of the work function of the film, so that PSQs having oligothiophenes will become good candidates of the above-mentioned layers in organic devices.

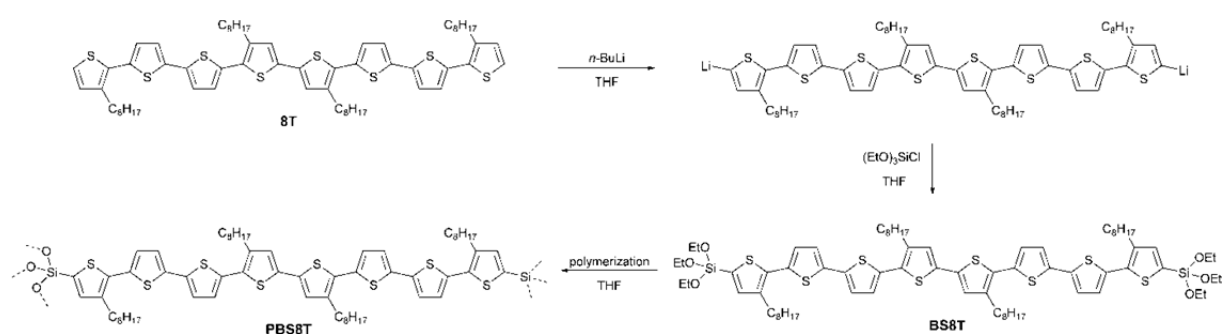
Herein, we report on the preliminary results on the synthesis of PSQ having octithiophene, along with optical, electrical and mechanical properties of the PSQ film anchored on glass and ITO substrates.

## 2. Experimental section

Octithiophene with two triethoxysilyl groups at the terminals, 3,3',4',3''-tetraoctyl-5,5''-bis(triethoxysilyl)-2,2':5',2'':5'',2''':5''',2''''':5''''',2''''':5''''',2''''''':5''''''',2''''''''':5'''''''''-octithiophene (BS8T) was synthesized as a monomer (Scheme 2). 3,3',4',3''-Tetraoctyl-2,2':5',2'':5'',2''':5''',2''''':5''''',2''''''':5''''''',2''''''''':5'''''''''-octithiophene (8T) was synthesized according to the literature [7]. Lithiation of 8T was carried out by 2 eq of *n*-butyllithium in THF at 0 °C for 30 min. Subsequently, the lithiated 8T was dropped into THF solution containing an excess amount of triethoxychlorosilane at 0 °C. The mixture solution was stirred at 0 °C for 30 min, and then at r.t. for 3 hr. The resulting crude product was purified by column chromatography, and characterized by <sup>1</sup>H NMR and FAB-MS.

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 0.88 (t, CH<sub>3</sub> in octyl, 6H, *J* = 7.7 Hz), 0.90 (t, CH<sub>3</sub> in octyl, 6H, *J* = 7.7 Hz), 1.26 (t, SiOCH<sub>2</sub>CH<sub>3</sub>, 18H, *J* = 6.8 Hz), 1.2-1.5 (br, methylene-*H* in octyl, 40H), 1.67 (tt, thienyl-CH<sub>2</sub>CH<sub>2</sub>, 4H, *J* = 7.7 Hz), 1.68 (tt, thienyl-CH<sub>2</sub>CH<sub>2</sub>, 4H, *J* = 7.7 Hz), 2.79 (t, thienyl-CH<sub>2</sub>, 4H, *J* = 7.7 Hz), 2.81 (t, thienyl-CH<sub>2</sub>, 4H, *J* = 7.7 Hz), 3.89 (q, SiOCH<sub>2</sub>CH<sub>3</sub>, 12H, *J* = 6.8 Hz), 7.06 (s, thienyl-*H*, 2H), 7.09 (d, thienyl-*H*, 2H, *J* = 3.9 Hz), 7.11 (d, thienyl-*H*, 2H, *J* = 3.9 Hz), 7.18 (d, thienyl-*H*, 4H, *J* = 3.9 Hz), 7.26 (s, thienyl-*H*, 2H). FAB-MS: *m/z* = 1431.5 (M<sup>+</sup>).

Polymerization of BS8T was carried out at r.t. for 6 hr in THF solution using a dilute hydrochloric acid (0.1M) as a catalyst. After polymerization, the resulting polymer (PBS8T) solution ( $M_n \sim 2500$ , estimated by GPC using polystyrene standard) was directly spin-coated on glass or ITO substrate (3000 rpm for 20 sec and then 5000 rpm for 10 sec), and the spun film was cured at 100 °C for 30 min and sonicated in acetone. Thicknesses of the PBS8T films were estimated to be ca. 60 – 80 nm by an atomic force microscopy (Agilent Technologies, 5500 Scanning Probe Microscope).



**Scheme 2.** Synthetic route of BS8T and PBS8T.

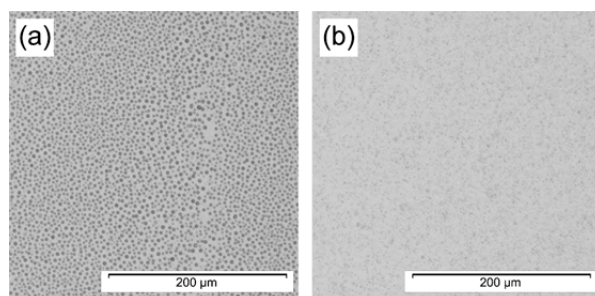
Film morphology was investigated by an optical microscope (Olympus, BX51). UV-Vis absorption spectra were measured by a spectrophotometer (Shimadzu, UV-3150). Cyclic voltammetry was carried out using a potentiostat/galvanostat (Hokuto Denko, HAB-151) with an X-Y recorder (Riken Denshi, F-57).

Hardness test of the PBS8T film was made according to the ASTM Standard D 3363-92, using a TQC Wolff-Wilborn tester (COTEC) with pencils of varying hardnesses (from 6B to 6H).

### 3. Results and discussion

To confirm the role of PSQ hybrid polymer (class II), the film morphology of PBS8T was compared with that of the film in class I obtained by the sol-gel method using a mixture of tetraethoxysilane (TEOS) and 8T. In the class I film, the sea-and-island morphology was

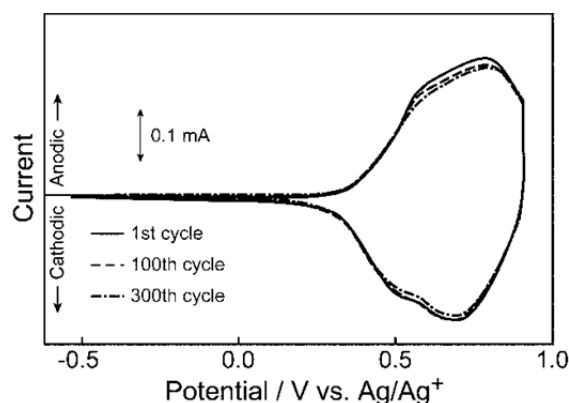
observed due to the phase separation between 8T (island) and SiO<sub>2</sub> from TEOS (sea) (Figure 1a). The phase separation is not favorable for electrical conduction, because conducting pathway is cut off due to the isolation of conductive 8T phases in the insulating SiO<sub>2</sub> matrix. It was also found that 8T was removed readily by dipping the sol-gel film into acetone, showing that the 8T molecules were just embedded in SiO<sub>2</sub> matrix with no formation of covalent bonds. On the other hand, the PBS8T film was very smooth and homogeneous (Figure 1b), and was insoluble in common organic solvents.



**Figure 1.** Optical microscopic images of the film obtained from TEOS and 8T (a), and the PBS8T film (b).

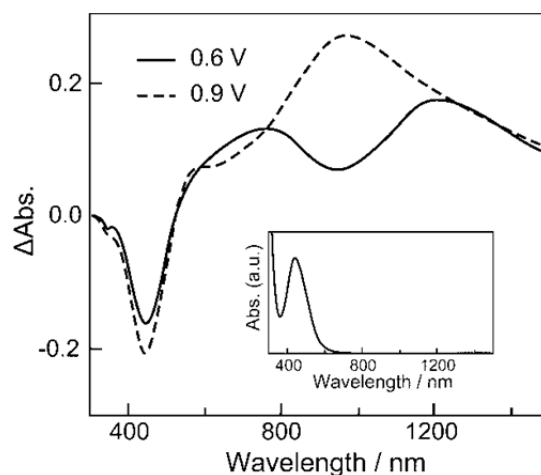
Stability of the PBS8T films was examined by cyclic voltammogram (CV) with the PBS8T-anchored ITO, Pt wire and Ag/Ag<sup>+</sup> as a working, counter and reference electrodes, respectively (Figure 2). Broad oxidation peaks were observed at 0.6 and 0.8 V vs. Ag/Ag<sup>+</sup>, corresponding to the first and second oxidation steps of octithiophene moiety in PBS8T, respectively. The reason for the broad peaks might be due to the low flexibility of octithiophene moiety tightly bound to the PSQ network. Even after the potential cycling between -0.5 and 0.9 V were repeated over 300 times, the shape of the CV curve was similar to that in the first cycle. Corriu et al. reported the synthesis and electrochemical properties of PSQs having oligothiophenes with short  $\pi$ -conjugation lengths (monomer to trimer) [8]. In their report, when their polymers were chemically or electrochemically oxidized,

oligothiophene moieties were eliminated and polymerized due to the low stability of the oxidized species. In contrast to their results, PBS8T showed a good electrochemical stability due to the delocalization of the formed charge in the moderate  $\pi$ -conjugation length, and a good adhesivity of the polymer to the ITO substrate.



**Figure 2.** Cyclic voltammograms of the PBS8T film on ITO electrode in  $\text{Et}_4\text{NClO}_4$  (0.1 M) / acetonitrile. Scan rate is  $50 \text{ mV sec}^{-1}$ .

Figure 3 depicts optical properties of PBS8T studied by spectroelectrochemistry with the PBS8T-anchored ITO as a working electrode. The neutral PBS8T showed a single absorption band at 450 nm due to  $\pi$ - $\pi^*$  transition of a neutral octithiophene moiety. When PBS8T was oxidized at 0.6V vs.  $\text{Ag}/\text{Ag}^+$ , the 450 nm band disappeared, and instead two absorption bands were newly observed at 750 and 1200 nm, which were ascribed to the one-electron oxidized species (monocation radical or  $\pi$ -dimer) of octithiophene. The PBS8T film oxidized at 0.9V vs.  $\text{Ag}/\text{Ag}^+$  showed a single broad band in the near infrared region centered at 950 nm, being ascribed to the two-electron oxidized species (dication) of octithiophene, and became almost colorless.



**Figure 3.** Difference absorption spectra of the PBS8T film on ITO biased at 0.6V (solid) and 0.9V (dashed) vs.  $\text{Ag}/\text{Ag}^+$ , referred to the spectrum of the neutral PBS8T (inset).

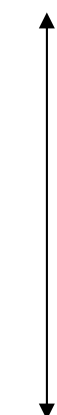
Electrical conductivity of the chemically oxidized PBS8T film by  $\text{FeCl}_3$  was measured by the two-probe dc method. When the polymer was dipped in  $\text{FeCl}_3$  solution, the electrical conductivity immediately increased from an insulating level to  $10^{-3} - 10^{-2}$  S/cm due to the charge formation by the chemical oxidation (doping), and this value was saturated a few minutes after dipping. Previously, we have found that the charge transport properties of oligothiophenes with long  $\pi$ -conjugation length (12–14 mers) are comparable to those of poly(thiophene)s [9]. This implies that the introduction of longer oligothiophenes into PSQs may lead to the formation of PSQ films having higher electrical conductivities. The absorption spectrum of the chemically oxidized PBS8T film showed absorption bands at 750 and 1200 nm, agreeing well with those for the one-electron oxidized species of octithiophene observed in the above-mentioned spectroelectrochemical experiments. Thus, at this oxidation condition, the polymer was only one-electron oxidized, so that the oxidized polymer film was not perfectly colorless and showed a slightly dark green color. The transmittance of the film was 60 – 70 % in the visible light region (350 – 850 nm) without light scattering. As is already shown in Figure 3, the PBS8T film in electrochemically two-electron oxidized state has no absorption in the visible region and the polymer film is visually colorless. Consequently, if the polymer could be two-electron oxidized by chemical oxidation as well,



more colorless and transparent polymer films might be obtained. By controlling the degree of oxidation, it is expected that electrical and optical properties can be improved. Such optimization of oxidation condition is now under investigation.

Finally, the mechanical strength of the film was measured by a pencil hardness test according to the ASTM Standard D 3363-92 [10] and the results are summarized in Table 1. The PBS8T film did not show any damages by scratching with 5H pencil. Even when 6H pencil is used, the PBS8T film showed a slight deformation, but was not peeled-off. In the cases of PEDOT-PSS and common polymer films such as poly(styrene) (PSt) and poly(methyl methacrylate) (PMMA), appreciable damages were caused even by soft pencils (2B for PEDOT-PSS and PSt, 2H for PMMA). From these results, it was found that the mechanical strength of the PBS8T film was much higher than those of polymers having no chemical linkage with substrates.

Table 1. Results of pencil hardness test for PBS8T, PEDOT-PSS, PSt, and PMMA<sup>a</sup>

Hardness of Pencil		PBS8T	PMMA	PSt	PEDOT-PSS
 (Hard)	6H	<i>D</i>			
	5H		<i>P</i>		
	4H				<i>P</i>
	3H		<i>D</i>	<i>P</i>	
	2H				
	H				
	F				
	HB	<i>N</i>			<i>D</i>
	B			<i>D</i>	
	2B		<i>N</i>		
	3B				
	4B			<i>N</i>	<i>N</i>
	5B				
	(Soft) 6B				

<sup>a</sup> *N*: no damage, *D*: plastic deformation (irreversible deformation, but no fracture), *P*: peeled-off.

In conclusion, a novel polysilsesquioxane having oligothiophene was synthesized and anchored successfully onto glass and ITO substrates by the spin-coating method. The hybrid

polymer was found to be smooth and homogeneous without phase separation. The oxidized PBS8T film showed a reasonably high electrical conductivity with an excellent mechanical strength. It is well-known that the energetic properties of polymer films can be controlled by changing the conjugation length and substituents of oligothiophenes [6]. So, the introduction of oligothiophenes with other conjugation length and substituents will tune the electrical properties as designed, which is now under investigation.

### **Acknowledgements**

This work was supported in part by grants from the Ogasawara Foundations for the Promotion of Science and Engineering (I.I.), and from the Tokuyama Science Foundation (I.I.), and a grant-in-aid for scientific research from the Japan Society for the Promotion of Science (JSPS) (no. 19350094, Y.H.).

The authors are grateful to Dr. Daisuke Kajiyama, the Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University for the measurement of FAB-MS.

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