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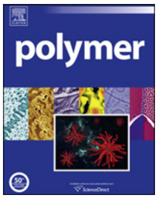

Polymer Communication

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 π-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.

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].

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

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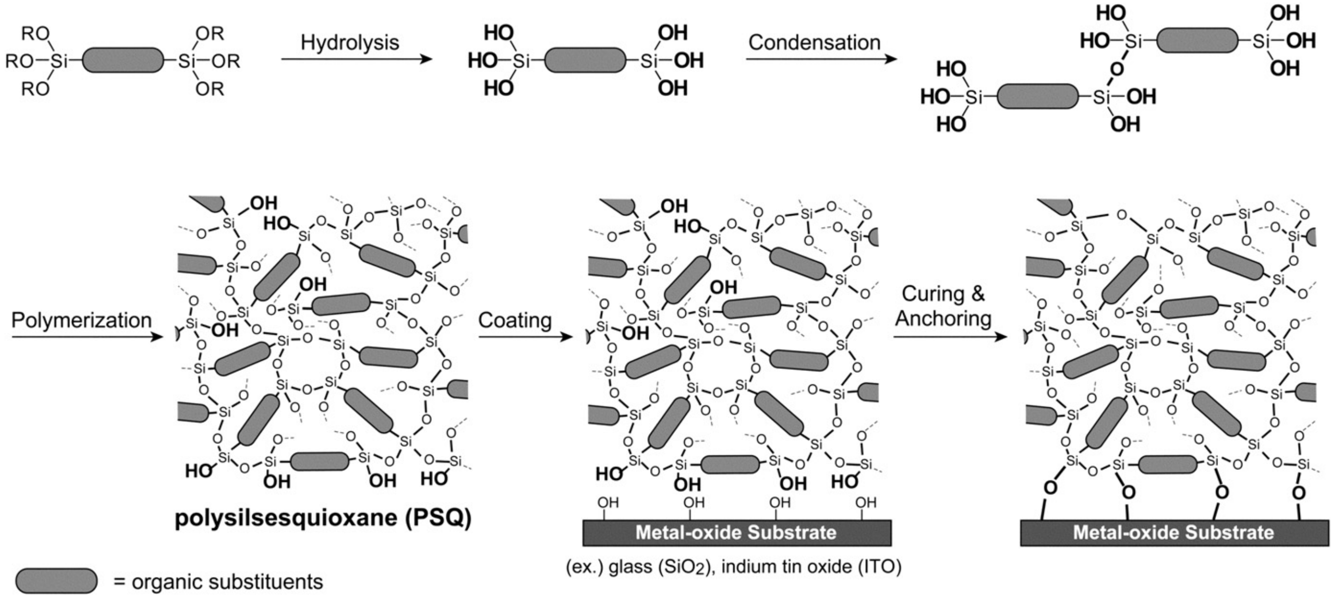


Scheme 1. Formation of polysilsesquioxanes by the hydrolysis and condensation of trialkoxysilyl-substituted monomers and their anchoring onto metal-oxide substrate.

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 π-conjugation length and by introducing electron donating or withdrawing groups on the π-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

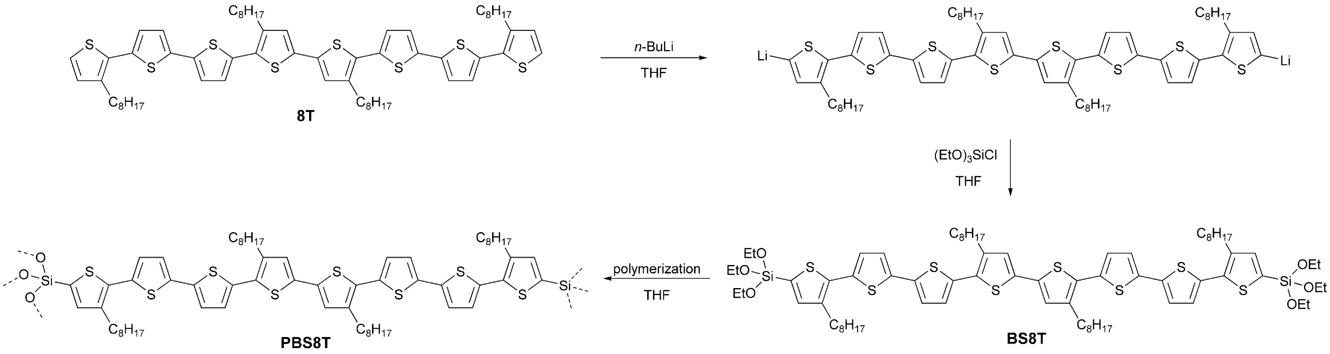
2.1. Synthesis of monomer

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′′′′′′′-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′′′′′′,2′′′′′′′-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 h. The resulting crude product was purified by column chromatography, and characterized by ^{1}H NMR and FAB-MS.

^{1}H NMR (CD_2Cl_2): $\delta = 0.88$ (t, $C\boldsymbol{H}_3$ in octyl, 6H, $J = 7.7$ Hz), 0.90 (t, $C\boldsymbol{H}_3$ in octyl, 6H, $J = 7.7$ Hz), 1.26 (t, $SiOCH_2C\boldsymbol{H}_3$, 18H, $J = 6.8$ Hz), 1.2–1.5 (br, methylene-***H*** in octyl, 40H), 1.67 (tt, thienyl-$CH_2C\boldsymbol{H}_2$, 4H, $J = 7.7$ Hz), 1.68 (tt, thienyl-$CH_2C\boldsymbol{H}_2$, 4H, $J = 7.7$ Hz), 2.79 (t, thienyl-$C\boldsymbol{H}_2$, 4H, $J = 7.7$ Hz), 2.81 (t, thienyl-$C\boldsymbol{H}_2$, 4H, $J = 7.7$ Hz), 3.89 (q, $SiOC\boldsymbol{H}_2CH_3$, 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^+).

2.2. Polymerization and anchoring

Polymerization of BS8T was carried out at r.t. for 6 h in THF solution using a dilute hydrochloric acid (0.1 M) 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 s and then 5000 rpm for 10 s), and the spun film was cured at 100 °C



Scheme 2. Synthetic route of BS8T and PBS8T.