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Preparation of surface initiated polystyrenesulfonate films and PEDOT doped by the films

Karen L. Mulfort, Jae Ryu, Qingye Zhou*

Elecon, Inc., 200 Turnpike Road, Chelmsford, MA 01824, USA

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Abstract

Various substrates such as glass slides and silicon wafers were modified by styrylethyltrimethoxysilane to attach double bonds to those surfaces. The double bond layer was initiated and capped by benzoyl peroxide (BPO) and 2,2,6,6-tetramethylpiperidirooxy (TEMPO), respectively, to form 'living' free radical layer from which polystyrene brushes were grown. The density of double bonds on the surface controlled the orientation of polystyrene brush or film. The polystyrene films were then sulfonated by fuming sulfuric acid ($H_2SO_4 \cdot xSO_3$) to obtain polystyrenesulfonic acid (PSS) films with controlled polymer chain alignment. The lower double bond density led to a lower degree of polymer chain alignment. 3,4-Ethylenedioxythiophene monomer was diffused into PSS film and then polymerized. A conductive polyethylenedioxythiophene (PEDOT)/PSS film was obtained. The films were characterized by four-point probe, AFM and UV–VIS. The conductivity of PSS/PEDOT film measured along the direction which is normal to polymer chain alignment, is lower than that from commercial PSS/PEDOT.

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Keywords: Surface initiated polymerization; Polystyrenesulfonic acid/polyethylenedioxythiophene; Conductive thin film

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1. Introduction

Conjugated conductive polymers have been used in many applications, such as polymer light emitting diodes (PLEDs) [1], organic transistors [2], smart windows, electronic paper, antistatic coating, sensors, batteries, solar cells, among others [3–6], One of the most important research fields is controlling the molecular and structural ordering of conductive polymers to improve their charge transport properties. McCullough [7] demonstrated that macromolecular self-assembly occurs with a properly designed polythiophene and leads to a large increase in electrical conductivity. Although carefully designed conductive polymers might show controlled structures, the syntheses are usually very complicated and costly. Most conductive polymers are insoluble upon synthesis. Therefore, branched polymers [8] and copolymers [9] were synthesized to improve the solubility. Other polymers were also used as dopants and emulsifiers to form very stable dispersions. The most commercially successful example is polyethylenedioxythiophene (PEDOT)/polystyrenesulfonic acid (PSS) system, which is very transmissive to visible light as well as highly conductive [10]. However, there is no way to construct the desired PSS structure throughout which PEDOT will be stacked in groups and randomly oriented. PSS coils and hosts PEDOT to form aqueous dispersion of PEDOT/PSS. Therefore, it is very hard to tune and investigate the effects of morphology and alignment of PSS on PEDOT/PSS properties.

Surface initiated polymerization is a promising and versatile method of preparing an assembly of tethered polymer chains forming 'polymer brushes'. This unique geometry originating at solid interfaces ideally results in end-grafted, strictly linear chains where the grafting density is sufficiently high with respect to the equilibrium radius of gyration (R_g) of the grafted macromolecules [11]. Thus, they will form highly oriented polymer chains as they are forced to stretch away from the interface due to steric crowding. The density of surface initiated polymer brushes (area per polymer chain occupied) could be controlled by varying the concentration of the initiator molecules in self-assembled monolayers [12]. Polymer brushes can be prepared by free radical [13] and living free radical [14]

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* Corresponding author. Tel.: +1-978-856-4211; fax: +1-978-250-4533. *E-mail address:* qzhou@eleconinc.com (Q. Zhou).

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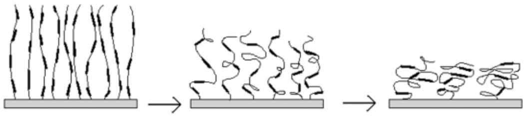
polymerizations, ring-opening metathesis [15] and atom transfer free radical [16] polymerizations, cationic [17] and anionic [18] polymerizations. All methods above have been shown to be suitable for polymerizing different types of monomers. Here, living free radical polymerization is used to obtain the desired architecture and uniform polymer brushes because of its living character and convenience.

Polystyrenesulfonic acid (PSS) brushes were prepared by an organic solvent soluble initiator/scavenger system such as benzoyl peroxide (BPO)/2,2,6,6-tetramethylpiperidirooxy (TEMPO) to polymerize styrene [19,20]. Surface initiated polystyrene films originating from silicon wafers have been successfully made using this method [14]. However, this polystyrene film has to be converted to polystyrenesulfonic acid film in a sulfonation step. 3,4-Ethylenedioxythiophene (EDOT) monomer was diffused into surface initiated polystyrenesulfonic acid films. With an appropriate catalyst, EDOT polymerized within these predesigned PSS films of various densities and alignments relative to the surface. PEDOT was formed and doped with PSS films. The alignment and morphology of PEDOT with PSS is controlled by PSS films as shown in Scheme 1 [21].



Scheme 1. Effects of initiator density on PEDOT/PSS conformation. Lines indicate PSS chain, black bars represent PEDOT.

2. Experimental section

2.1. Materials

3,4-ethylenediethoxythiophene as Baytron M was purchased from Bayer AG, used as received. Styrylethyltrimethoxysilane and phenethyltrimethoxysilane were obtained from Gelest, used as received. Styrene was obtained from Sigma–Aldrich and vacuum distilled before use. Ethylene glycol, iron (III) chloride ($FeCl_3$), dichloroethane, xylene, BPO, TEMPO, phenethyltrimethoxysilane, hydrogen peroxide and fuming sulfuric acid ($H_2SO_4 \cdot xSO_3$) were purchased from Aldrich, used as received. Commercial product of PSS/PEDOT as Baytron P was purchased from Bayer AG, this material was coated on the substrate to compare with surface initiated PSS/PEDOT systems.

2.2. Characterization

Number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity indices (M_w/M_n) were determined by size exclusion chromatography (SEC) relative to calibration with polystyrene standards in THF. SEC in THF (flow rate, 1 ml/min; Waters styragel 100, 500, 10^3, 10^4, and 10^5 Å columns) was obtained by using a Waters 510 pump with a Waters 410 differential refractometer detector. FTIR spectra were obtained from a Bruker FTIR from 4000 to 600 cm^{-1}. FTIR samples were obtained by polymerizing styrene on IR transparent silicon wafer surfaces. Ellipsometric thickness measurements were performed using the Multiskop ellipsometer (Optrel GmbH, Germany) with 632.8 nm He–Ne laser beam as the light source. Both delta and psi values (thickness data) were measured and calculated using integrated specialized software that is standard with the instrument. Atomic force microscopy (AFM) imaging was performed in air using a PicoScan system (Molecular Imaging) equipped with an $8 \times 8\ \mu m^2$ scanner. Contact angle measurements were done on a MIcroCAM contact angle goniometer. The measurements were taken at several different spots of the same sample and the average value reported. The surface resistance of PEDOT/PSS films was measured by Keithley Electrometer, Model 6517, with a four-point probe method. UV–VIS spectra were investigated with DT-1000CE UV–VIS spectroscopy of Analytical Instruments Systems, Inc. in a range 200–850 nm.

2.3. Immobilization of initiator precursor

Silicon wafers and glass slides were cleaned by a mixture of sulfuric acid and H_2O_2, then thoroughly rinsed by deionized water and dried overnight at 120 °C. Dried surfaces were immediately transferred to a 0.1 mmol solution of styrylethyltrimethoxysilane (initiator precursor) in toluene for 24 h to attach the double bonds to the surfaces by silane chemistry. After reaction, the substrates were thoroughly rinsed by toluene and acetone in sequence. A styrene-like initiator precursor monolayer was obtained to form a 'free radical layer' after the reaction of double bonds with the initiator/scavenger system of BPO/TEMPO.

2.4. Preparation of polystyrenesulfonic acid films

We focus on styrene polymerization procedure initiated by BPO/TEMPO in organic solvent and conversion of polystyrene films to PSS films by sulfonation.[1] Substrate (glass or Si–wafer) with an initiator precursor layer was placed in a 250 ml three-neck round bottom flask equipped with a condenser and covered with 150 ml xylene. With stirring, 0.05 mmol (0.015 g) BPO and 0.1 mmol (0.017 g) TEMPO were added. The system was heated to 130 °C under nitrogen by oil bath. The double bonds were initiated by BPO and capped by TEMPO to form a 'living free radical' layer, from where polystyrene can grow. The living free radicals of TEMPO derivatives have been directly

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[1] We also initiated surface polymerization of styrene monomer by $K_2S_2O_8$/3-carboxyl-PROXYL. However, poor compatibility of hydrophobic surface of substrate and hydrophilic solvent and initiator/scavenger system caused the bubbles on the intersurface between substrate and solvent, which gave less uniform polymer films.

attached to surfaces by other groups [14a]. However, very complicated synthesis procedures must be involved. We have demonstrated that double bond modified surfaces can be successfully initiated by anionic initiator to anionically polymerize styrene films from various substrates [18,22]. A similar idea was cited here. After polymerization was completed, the substrates with polystyrene film were sonicated five times, 15 min each in toluene to remove any free polystyrene chains. Free polystyrene in solution was precipitated into methanol and dried under vacuum. The samples were analyzed by SEC to determine molecular weight and polydispersity. The polystyrene-covered substrate was then placed in a 250 ml three-neck flask and covered with 150 ml dichloroethane. Fuming sulfuric acid (1.5 ml) was added at room temperature to sulfonate the polystyrene film on the surface. FTIR and surface contact angle were followed throughout the reaction to determine the degree of sulfonation.

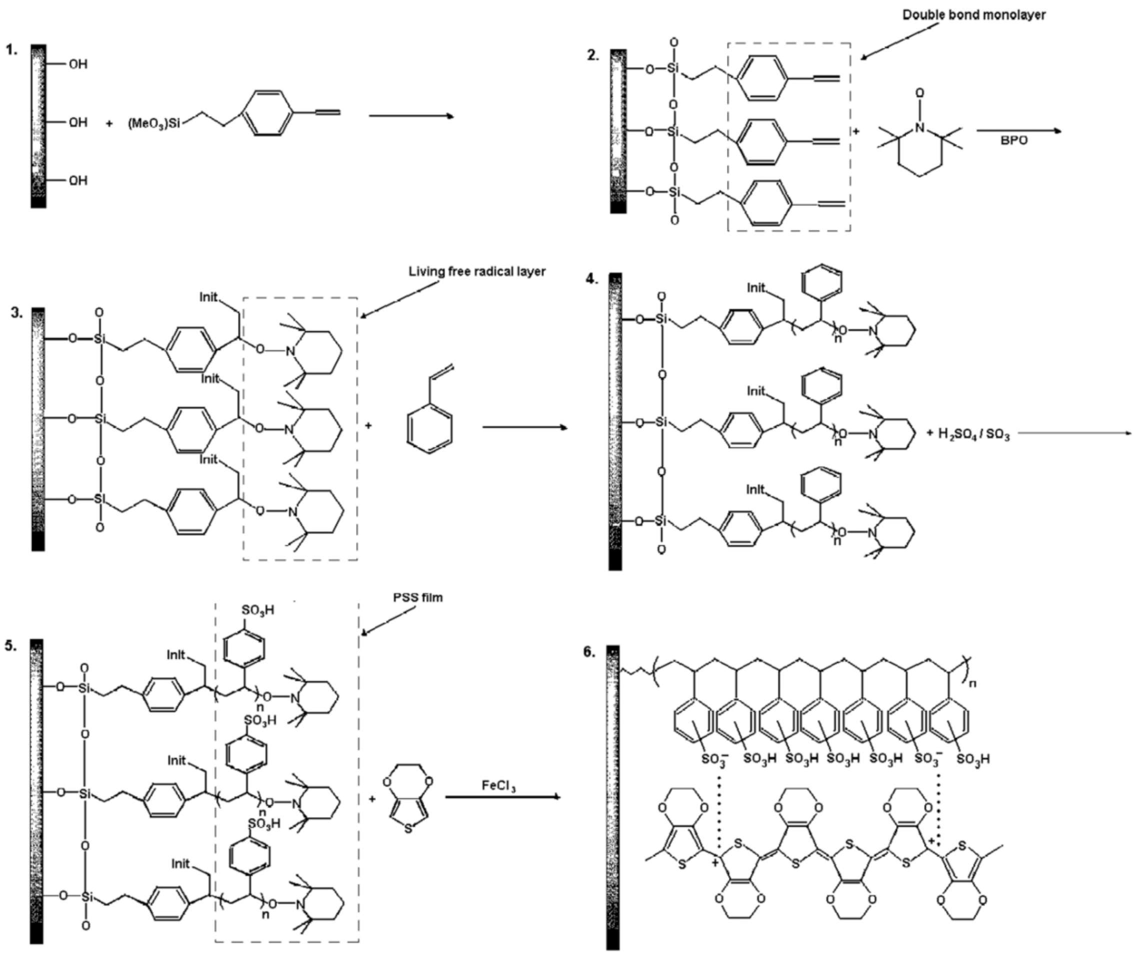
2.5. Polymerization of EDOT in polystyrenesulfonic acid films

The polystyrenesulfonic acid film substrate was placed in a 250 ml round bottom flask and covered with 150 ml deionized water. Under nitrogen, 0.5 g EDOT was added and stirred overnight to allow the monomer to diffuse into the PSS film. $FeCl_3$ (2 g) was then added to polymerize EDOT. The surface of substrate quickly turned blue while solution remained yellowish. The reaction was allowed 2 days to complete. After reaction, the substrate was sonicated five times, 15 min each in deionized water to remove the catalyst and other physical adsorptions. A clear blue film was obtained on the substrate surface. The reaction scheme is shown in Scheme 2.

3. Results and discussion

A simplified living free radical polymerization method was employed to make polystyrenesulfonic acid film from substrate surfaces. Instead of using costly TEMPO derivatives, commercially available styrylethyltrimethoxysilane was attached to substrate surfaces to form a double bond monolayer as shown in Scheme 2. This monolayer showed a thickness of about 1.5 nm, as measured by ellipsometric methods. The double bond layer was initiated by BPO and capped by TEMPO to obtain a ‘living free radical’ layer, also shown in Scheme 2. Excess BPO was used to ensure initiation of all possible double bonds present on the surface. Actually, predetermined amounts of ‘free’ initiator were suggested to improve surface initiated polymerization control [14a]. After initiating the double bonds with the BPO/TEMPO system for 4 h, styrene monomer was added to the reactor to grow polystyrene from the surface. Polystyrene also grew in the solution because of the existence of excess BPO/TEMPO. For comparative purposes, a small amount of styrene monomer (mole ratio of 0.9/1 of styrene/BPO) was added to the reactor with the initiator/scavenger system, before adding the rest of the monomer. Therefore, BPO initiated double bonds on the surface as well as styrene monomer in the solution for four hours. Capped by TEMPO, the BPO–styrene–TEMPO system remained in solution. It was thought that the addition of styrene monomer would result in a more stable system than BPO/TEMPO in solution alone due to the free radical stabilization over the benzene ring. However, results did not show any difference between systems with or without additional monomer during the initiation procedure and after polymerization of rest of monomers. Polymer grew from both the immobilized surface initiator and soluble initiators. Any polymer formed in solution was easily removed from the substrate by washing with the appropriate solvent. Usually, repeated sonication of substrate with the polymer film in toluene completely removes any non-covalently bound polymer. Initiator efficiency will be limited with increasing surface density of BPO initiated double bonds due to steric hindrance. However, low initiation efficiency has been observed [12,23] even when initiators were attached directly to the substrate. It has been demonstrated that the molecular weight of the covalently bound polymer is related to the molecular weight of the ‘bulk’ polymer [14a,22b,24]. As shown in Fig. 1, the molecular weight of bulk polymer increases almost linearly with the ratio of styrene to initiator. This demonstrates that the chain growth from the surface is a relatively controlled process with ‘living’ character. It can be predicted that the brush thickness of polystyrene on the surface is controlled by the monomer/initiator ratio or polymer molecular weight. Fig. 2 shows that polymer film thickness increases linearly with the molecular weight of bulk polymer, except at very low molecular weights or very thin polymer films. All of these results agree nicely with previous conclusions from other authors [14a]. Polymerization in the bulk solution and from the substrate surface can be controlled due to its living nature. As can be seen in Fig. 3, SEC data shows a lower molecular weight tail that was also observed in other surface initiated polymerization methods [22a,24]. This was explained by Husseman et al. [14a] as a characteristic of TEMPO mediated ‘living’ free radical polymerizations. The comparison of the SEC traces for ‘cleaved’ polystyrene from the surface and the ‘bulk’ polystyrene from the solution is not available in this work due to small surface area of substrate, which cannot supply enough materials for SEC tests. All polymers have polydispersity indices from 1.6 to 1.8, which is higher than a polydispersity of 1.2 found from a similar method [14a]. No clear reason for this discrepancy can be concluded [22a,24] from experimental data. However, it can be hypothesized that the effect of the half life time of BPO should be taken into account when holding the BPO/TEMPO system at 130 °C for 4 h.

It has been demonstrated that surface initiated polymer



Scheme 2. Schematic diagram of initiator immobilization, activation of double bonds and polymerization of styrene and PEDOT.

growth is affected by steric factors [24]. A cross-sectional area per chain, A_x, can be calculated by the molecular weight of the chain and the corresponding film thickness, by the following equation:

$$A_x = M/t_\rho N_A$$

where M is the molecular weight of chain, t is film thickness, ρ is the mass density (1.05 g/cm^3 for polystyrene) and N_A is Avogadro's number. An average value of A_x of 200 Å^2 was obtained from previous work of surface initiated living free radical polymerization. However, we have a broader value of 298–350 Å^2 (lower density of polymer on the surface), which is much higher than 200 Å^2 (higher density of polymer). This is most likely due to poor initiator efficiency. Even though very reproducible results were obtained from the bulk polymerization, there may be a larger variation in molecular weight of the surface initiated polymer from batch to batch. Another factor that might affect the polymer surface density is that we used BPO/TEMPO to initiate double bonds and polymerize monomer instead of a directly attached TEMPO derivative. The space hindrance of BPO/TEMPO may reduce the initiator efficiency on the surface. However, even 100% directly

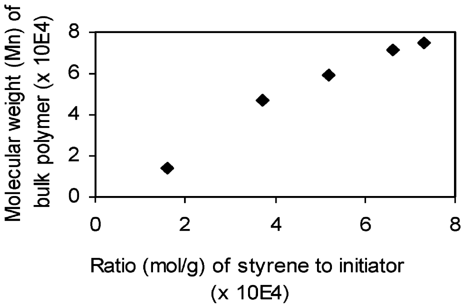


Fig. 1. Relation between amount of monomer and molecular weight of bulk polymer.

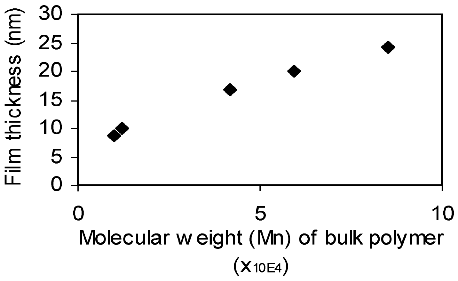


Fig. 2. Polystyrene thickness increases linearly with molecular weight of bulk polymer formed in solution.

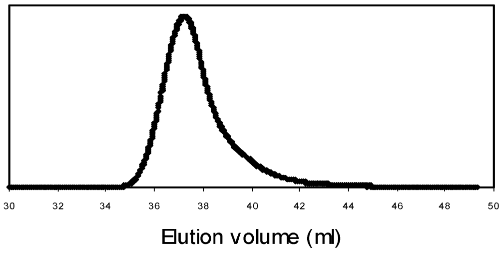


Fig. 3. SEC trace of bulk polymer obtained from the polymerization of a mole ratio of 6.60×10^4 of monomer to initiator.

attached initiators also showed only around 10% initiation efficiency [12], so it is not very clear what caused the difference of polymer densities from our work and others. A different initiator density was used to investigate the initiator density effects on surface initiated polymerization and the alignment of polymer chains. A 50/50 mixture of styrylethyltrimethoxysilane (active initiator precursor) and phenethyltrimethoxysilane (inert additive) was used to make a monolayer on the substrate. This has been done by first preparing a solution of the mixture of styrylethyltrimethoxysilane (active initiator precursor) and phenethyltrimethoxysilane (inert additive) at various mole ratios. Cleaned substrate was then submerged in this solution as usual. Both active initiator precursor and inert additive will react to the surface. Therefore, various density of active initiator precursor of styrylethyltrimethoxysilane can be obtained. Only active initiator precursor can be initiated by BPO/TEMPO. The same procedure was used to polymerize styrene as 100% active initiator precursor on the surface. The polymers obtained from bulk solution showed similar molecular weight and polydispersity as with 100% active initiator precursor on the surface. When the same monomer/initiator ratio was used, the film thickness was lower and the cross-sectional area per chain was higher than with 100% active initiator. The range of A_x for 50% active initiator is about 420–550 Å^2. It did not show the low efficiency of 10% as reported elsewhere, but it is clear to see the effect of density of active initiator precursor on alignment of surface initiated polymer chains. Compared to the cross-sectional area of 900 Å^2 of a polystyrene chain anchored to the interface by other means, our polymer chains, either from 100% active initiators or 50%, are very much stretched away from the substrate. This indicates that by changing the initiator density, the alignment of polymer chains from the surface can be relatively easily controlled.

The polystyrene films initiated from the substrate must be converted to polystyrenesulfonic acid films to accomplish the goal of this work. This can be done by sulfonation of the polystyrene films with fuming sulfuric acid. Contact angle results showed that 3 h are sufficient to obtain a fully sulfonated polystyrene (PSS) film as shown in Fig. 4. This is supported by FTIR spectra that showed –SO3 antisymmetric and symmetric stretching vibrational bands around 1200 and 1050 cm^{-1}, respectively, after sulfonation of the polystyrene films.

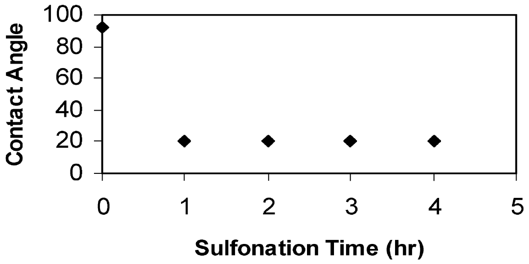


Fig. 4. Contact angle vs. sulfonation time.

After a certain time of sulfonation of polystyrene film in a fuming sulfuric acid solution in dichloroethane, samples were placed in deionized water and sonicated several times. This ensured the complete removal of all free sulfuric acid remaining on the surface. Then EDOT was added to water containing the polystyrenesulfonic acid film substrate and allowed to diffuse into the PSS film. The solubility of EDOT in water is very low (2 g/l, 20 °C); therefore, the interaction between PSS and EDOT will drive more EDOT into the films to reach equilibrium. EDOT in PSS film was allowed to polymerize with $FeCl_3$ and formed PEDOT. At several steps during this procedure, the contact angle of the substrate was measured. As shown in Fig. 5, the contact angle changed after the various treatments. After washing by the mixture of H_2O_2 and sulfuric acid, the contact angle reduced from about 40–20°. The contact angle went up to 66° after initiator precursor styrylethyltrimethoxysilane was added. There was no significant difference when 50% styrylethyltrimethoxysilane was used. Polystyrene film showed highest contact angle of 91°. Sulfonated polystyrene film showed very low contact angle, almost the same as H_2O_2 and H_2SO_4 treated glass surface at 20°. After diffusing and polymerizing EDOT in PSS film, the contact angle increased again to 82°. This indirectly indicates the structure change of the polymer surface with each treatment.

Because there is a lack of refractive index of the PSS film alone, we did not measure the change of PSS film before and after EDOT polymerization. However, a blue transparent film, which cannot be removed by sonication in water, implies that EDOT polymerized in PSS film successfully. After adding $FeCl_3$ to PSS film/EDOT system, the blue color appeared on the substrate surface much earlier than in the solution. The film morphologies of PSS/PEDOT are shown in Fig. 6. The thinner PSS/PEDOT film seems to give a rougher surface than the pure initiator surface. Surface roughness is improved by increasing the film thickness.

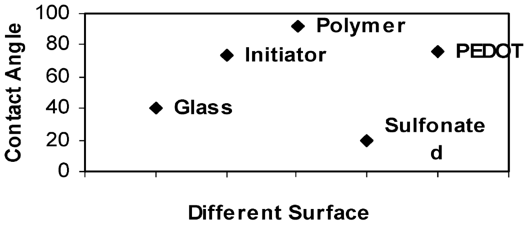
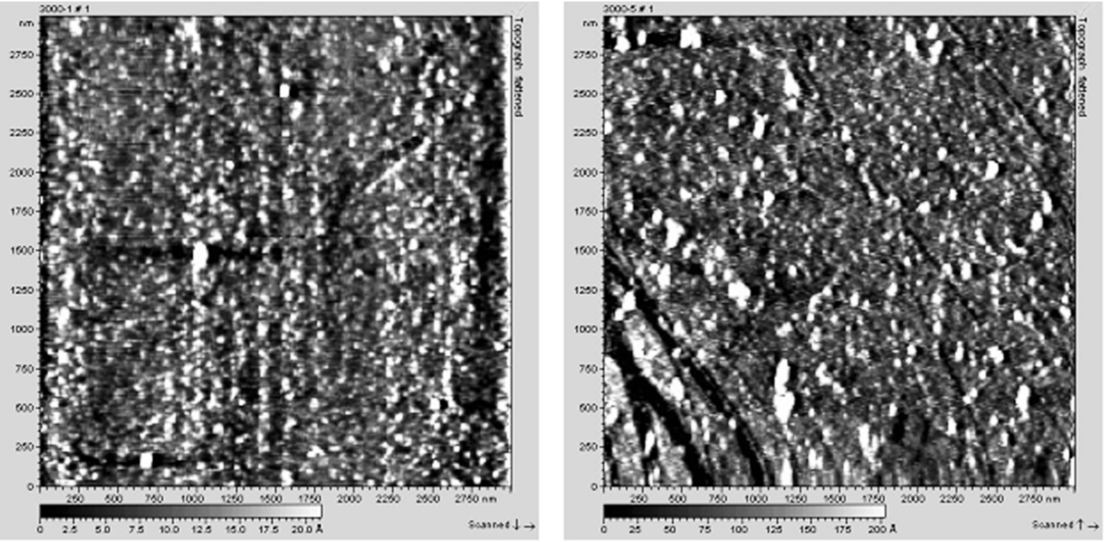
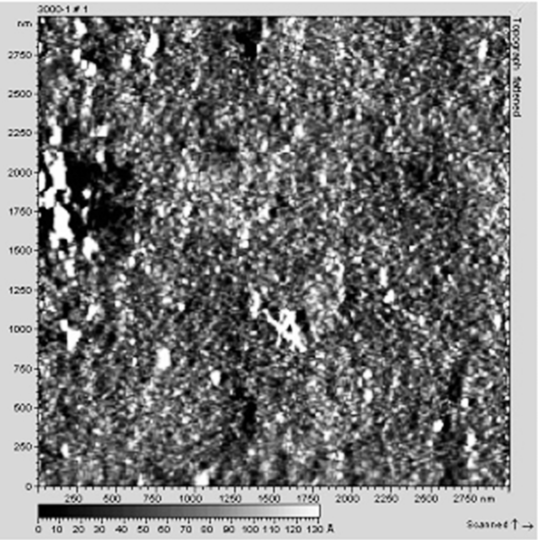


Fig. 5. Contact angle of various surfaces of substrates.



Initiator surface **10.8nm PSS/PEDOT**



23.4nm PSS/PEDOT

Fig. 6. AFM images of PSS/PEDOT films.

It is important to investigate the effects of alignment of PSS/PEDOT films on their conductivity. The conductivity of the film was determined by the four-point probe method. As can be seen in Table 1, at similar thicknesses, surface initiated PSS-doped PEDOT shows lower conductivity than a spin coated PSS/PEDOT emulsion in which the most of PSS/PEDOT particles are aligned parallel to the substrate. The comparison of different film alignments was achieved by evaluating various densities, or cross-sectional areas, of the PSS film. Here, alignment signifies the degree of orientation of the polymer chains along the direction normal to the surface. Higher alignment (lower cross-sectional area) represents that polymer chains are more stretched away from the surface. Table 1 shows the higher alignment of PSS chain leads to the lower conductivity of PSS/PEDOT. The conductivity is the reciprocal of resistivity, which in turn is

Table 1
Effects of polymer chain alignment on conductivities of PSS/PEDOT films

	Density of double bonds (%)	Thickness (nm)	Cross-sectional area/chain (Å)	Surface resistance (lΩsc)
KMSP5	100	19.7	298	760
KMSP8	100	234	310	748
KMSP7	50	188	428	560
KMSP11	50	226	456	568
PSSPEDOT	BaytronP	229		396

proportional to surface resistance. When 50% active initiator precursor (double bonds) was used, the resulting PSS films show a lower alignment of polymer chain than PSS films initiated with 100% active sites. For example, a PSS/PEDOT film, obtained from 50% active initiator precursor with a cross-sectional area of 456 Å^2, has a surface resistance of 568 kΩ/square. Comparatively, a PSS/PEDOT film obtained from 100% active initiator with a cross-sectional area of 310 Å^2 shows a surface resistance of 748 kΩ/square. We conclude the results as the effects of alignment of PEDOT along with PSS. When EDOT diffused into PSS, the monomer will try to stay along PSS chain due to entropy limitations. When EDOT polymerizes, a few PEDOT chains may stack into a fibril bundle. Those fibril bundles would prefer to keep along the axis parallel to PSS chain alignment because of their doper (PSS) and acceptor (PEDOT) nature and entropy requirement as well. Four-point probe measured the conductivity along the horizontal direction in which charges transfer through the interfaces for many fibril bundles of PEDOT doped by PSS. Therefore, a lower conductivity, or higher surface resistance, was obtained compared to that along the direction of polymer chain alignment. More direct evidence is needed to discuss the detailed mechanism of the alignment effects on the conductivity. The measurements of conductivity along the direction of polymer chain alignment and normal to that direction would be very illustrative. UV–VIS reveals no significant change between a commercial PSS/PEDOT (Baytron P) and surface initiated PSS/PEDOT. Polarized UV–VIS spectra should be done to record the transmitted light both in parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) directions with respect to the direction of polarization. The anisotropy of conductivity can then be detected.

4. Conclusion

The double bonds were attached on the substrates, sequentially initiated and capped by BPO and TEMPO, respectively. By this simplified method, polystyrene films were made by surface initiated living free radical polymerization of styrene. Polystyrenes obtained from the above method showed a higher polydispersity with regard to published data. A larger cross-sectional area occupied per polymer chain was also observed. This most likely results from the initiation efficiency of the double bonds on the surface. Control of the polymer chain alignment was accomplished by varying the density of double bonds on the surface. PSS films were obtained by the sulfonation of polystyrene films. EDOT monomers then diffused into the surface initiated PSS films and were polymerized to form PEDOT doped by PSS films. Surface initiated PSS/PEDOT films showed lower conductivity than those from commercial PSS/PEDOT coatings at roughly same thickness, measured by the four-point probe method. This discrepancy was identified as the effect of alignment of PSS chains, which doped and hosted PEDOT. EDOT polymerized along the direction of alignment of the PSS chains and should show better conductivity in the same direction. However, when measured by four-point probe method, only conductivity normal to PSS/PEDOT alignment direction was detected, resulting in a lower conductivity measurement. This is an indirect evidence that better alignment of PSS/PEDOT gives higher conductivity along its alignment direction.

Acknowledgements

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