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Intermolecular segregation of siloxane in P3HT: surface quantification and molecular surface-structure

M.W.G. Ponjée[a], M.A. Reijme[a], A.W. Denier van der Gon[a], H.H. Brongersma[a,*], B.M.W. Langeveld-Voss[b]

[a]*Physics of Surfaces and Interfaces, Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*
[b]*Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

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Abstract

Surfaces of spin-coated and solution-cast poly(3-hexylthiophene) (P3HT) films are analysed by X-ray Photoelectron Spectroscopy and Low Energy Ion Scattering. Here, we use the P3HT–siloxane system with only 2% siloxane monomers in the bulk as a model system to study segregation and surface orientation of molecules in polymers. The surfaces are enriched in siloxane due to the intermolecular segregation of the siloxanes present in P3HT. The siloxane coverage fraction was found to depend on the preparation parameters such as spinspeed and solution-concentration, and ranges from 25 to 100%.

The molecular orientation of segregated siloxanes on P3HT was found to resemble that on pure PDMS. Furthermore, siloxane molecules prefer specific sites on P3HT, such that sulphur atoms are screened from being at the outermost surface to lower the surface free energy. The results presented here demonstrate clearly the unique ability of LEIS to quantify the composition of the outermost atomic layer, and to obtain detailed information on the surface structure. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Low Energy Ion Scattering (LEIS, ISS); Poly(3-hexyl)thiophene-siloxane)(P3HT-DMS); Intermolecular surface segregation

1. Introduction

1.1. General

Since the end of the seventies conjugated polymers are studied in view of their potential technological applications, which have clearly been demonstrated by the fabrication of organic electronic devices such as Field Effect Transistors (FETs) and Polymeric Light Emitting Diodes (PLEDs) in which polythiophene or polyphenylenevinylene constituted the active component [1,2]. Polythiophenes constitute a particularly important class of conjugated polymers [3,4] due to their high chemical stability, high resistivity to heat [5] and non-degenerate electronic ground state. Since their first synthesis in 1986, poly(3-alkylthiophenes) have attracted increasing interest owing to their significantly improved solubility. This enables the use of straightforward methods for film preparation [6,7], such as spin coating and solution casting. Poly(3-hexylthiophene) (P3HT) belongs to this class of poly(3-alkylthiophenes). In a recent publication [8] thin-film field-effect transistor structures, consisting of P3HT/SiO_2/Si, were used as a model to show the possibility of achieving high mobility via two-dimensional transport in self-organised conjugated lamellae. This is important for applications of polymer transistors in logic circuits and active-matrix displays. An extensive review about conjugated polymers in general, including thiophenes, can be found in the handbook edited by Nalwa [4].

In many applications in which polymer films are used the chemical and physical properties of organic surfaces and interfaces play a key role in the performance. Properties such as chemical reactivity, adhesion, reflectivity and degradation, depend strongly on the surface composition. It is often assumed that the polymer surface composition reflects the repeating chemical unit in a polymer, yet deviations from this can be present due to preferred orientations of functional groups and chain-conformations at surfaces or due to segregation of additives and impurities [9]. Hence, the properties of a polymer surface can differ significantly from those expected on the basis of the average bulk composition.

In this paper we report a surface study of thin spin-coated and solution-cast films of P3HT which contains a low concentration of siloxane. Low Energy Ion Scattering (LEIS) was used to probe the composition of the topmost

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* Corresponding author. Tel.: +31-402-474-281; fax: +31-402-453-587.
E-mail address: h.h.brongersma@tue.nl (H.H. Brongersma).

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atomic layer and to obtain information about the molecular surface-structure, while X-ray Photoelectron Spectroscopy (XPS) was used as a complementary technique to determine the composition of the surface region. The siloxane–P3HT system is interesting in itself (siloxanes are often present as impurities in polymers), but is was also chosen as a model system to demonstrate the unique capability of LEIS to quantify the surface composition of mixed systems, and to obtain information on the position and orientation of molecules present at surfaces of organic materials.

1.2. Surface techniques XPS and LEIS

XPS is the most commonly used technique to study polymer surfaces. XPS provides both a quantitative analysis of the surface region composition and information about the chemical state of the atoms. This information is extracted from the kinetic energy distribution of photo-electrons emitted by the sample, which is irradiated by a monochromatic X-ray beam. The information depth of XPS is determined by the mean free path of the photoelectrons, and is typically 50–100 Å in polymers (about three times the mean free path of the photoelectrons). The surface sensitivity can be enhanced significantly by employing a glancing exit angle, but the information always originates from a region much deeper than the outermost atomic layer. Extensive literature is available with more information on the principles of XPS [10–12] and its application on polymers [13,14].

In contrast to XPS, LEIS has only been sporadically employed for the investigation of polymer surfaces. LEIS has an extremely high surface sensitivity and probes only the composition of the outermost atomic layer [15,16]. In LEIS a monoenergetic beam of noble gas ions (like He^+, Ne^+, Ar^+) with the energy of typically 1–5 keV is directed at the target surface where the ions are scattered. Measurement of the kinetic energy spectrum of elastically backscattered ions allows determination of the mass of the surface atoms from which the ions were scattered, and the energy spectrum thus resembles a mass spectrum of the outermost atomic layer. Depth profiles can be obtained by means of sputter-profiling, although it should be kept in mind that the depth resolution is limited by the statistics of the sputtering process, in particular by effects such as mixing, selective sputtering and surface decomposition.

Due to screening effects — shadowing and shielding [15,17,18] — and its high surface sensitivity LEIS is also structure sensitive [19] and possesses the capability to study the preferential orientation of groups and chain conformations at organic surfaces [16–18,20–26]. For details about the principles of LEIS the reader is referred to literature [17,27,28], and in particular for the study of polymer surfaces using LEIS to the work of the 'Gardella' group [17,21–26,29].

Although LEIS is routinely used in studies of inorganic materials, it is rarely applied to study polymer surfaces. LEIS is essentially a destructive technique and causes damage that can influence the surface composition, such as the loss of surface particles, implantation of ions and recoils, lattice destruction, amorphisation, bond breaking and bond formation [30–32]. Hence, a low ion dose has to be used during LEIS experiments, such that so-called 'static' conditions are obtained, i.e. the measured surface composition is not influenced by the measurement itself. Therefore, a very sensitive analyser–detector system is necessary, in addition to lowering the ion dose by rastering the ion beam across the surface, to obtain enough counting statistics while maintaining 'static' conditions.

2. Experimental

The monomer used to synthesise P3HT has been prepared by reacting 3-bromothiophene with the Grignard reagent of hexylbromide and a catalytic amount of $Ni(dppp)Cl_2$ [33,34]. Subsequently, P3HT was prepared by oxidative polymerisation using iron(III) chloride [35]. Fig. 1 schematically shows the chemical structure of the thus obtained P3HT. The polymers consist of on average 100 coupled monomeric units, with 75 regioregular Head-to-Tail couplings. Further detailed information about the synthesis route of P3HT can be found in Ref. [35]. The synthesized P3HT was shaped into a free-standing film by means of solution casting, which was used to prepare various series of thin films. Using Proton Induced X-ray Emission (PIXE) and RBS a low bulk concentration of siloxane was detected in the as-synthesized P3HT. The number of siloxane monomers was found to be equal to 2% of the number of P3HT monomers. The composition of the siloxane was determined with XPS and found to be H_xC_2SiO (hydrogen is undetectable), which resembles that of dimethylsiloxane — $(CH_3)_2SiO$ (DMS).

Si(100) p-doped wafers (1×1 cm^2) with a native oxide

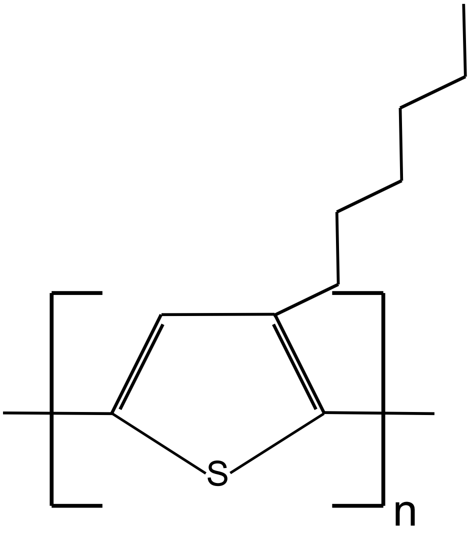

Fig. 1. Chemical structure of poly(3-hexylthiophene).

layer were used as substrates for solution casting and spin coating of P3HT films. Prior to deposition of P3HT, the substrates were ultrasonically cleaned in ethanol for 15 min. Solution casting and spin coating were performed in ambient atmosphere at room-temperature with solutions consisting of P3HT dissolved in toluene (concentrations ≤8.7 mg/ml P3HT/toluene). P3HT films were prepared with spinspeeds varying between 4×10^3 and 15×10^3 rpm. The thickness of films was measured with a Tencor Alpha-step 100 profilometer.

LEIS measurements were performed in a UHV system (ERISS) with a base pressure of 2×10^{-10} mbar. In the ERISS set-up, the kinetic energy of ions (back)scattered by 145° is analysed and detected by a double toroidal analyser and position-sensitive detector [36]. Due to the high detection efficiency of this analyser–detector system and the rastering of the ion beam across the sample surface, 'static' LEIS was performed with an ion dose as low as 1×10^{13} ions/cm^2. To prevent charging, the samples were flooded with low energy electrons. The LEIS measurements were performed using 3 keV ^{3}He$^+$ and 4.75 keV ^{4}He$^+$ ions and a current typically in the range of 0.3–1 nA. The LEIS spectra were analysed by determination of the peak areas after linear background subtraction.

XPS measurements were performed in the same set-up with MgKα (1253.6 eV) X-rays, produced by a VG Scientific type 427 Twin Anode. Photoelectrons emitted from the target were recorded with an energy resolution of 2.0 eV (FWHM of 3d$_{5/2}$ Ag peak) by means of the same analyser–detector system as used in LEIS. The spectra were analysed by determination of peak areas, which were used together with listed elemental sensitivities to calculate relative elemental ratios, and it was verified that these sensitivity factors gave the correct ratios for a pure PDMS sample.

3. Results and discussion

3.1. Intermolecular segregation of siloxane in P3HT

Fig. 2a shows the LEIS spectrum of a spin-coated P3HT film (spinspeed 7.3×10^3 rpm, solution-concentration 7.1 mg/ml P3HT/toluene) and indicates the presence of carbon, oxygen, silicon and sulphur in the outermost surface. The low contribution of sulphur to the high-energy peak was determined by means of curve fitting. The intense background sputterpeak at low energies is due to sputtering of light and loosely bound particles such as hydrogen [18,20,37–39]. Since the spin-coated P3HT layers are fully closed and LEIS spectra of thick (several (m) solution-cast P3HT films (Fig. 2b) also show clear oxygen and silicon signals, it is concluded that siloxane molecules in P3HT segregate towards the surface. This is supported by the LEIS spectrum of pure PDMS (Mn = 18 kg/mol) (Fig. 2c), as it looks similar to that of the solution-cast P3HT film (Fig. 2b). Comparison between Fig. 2a and b shows that the silicon and oxygen LEIS signals of the solution-cast film are more intense than those of the spin-coated film. In addition, no sulphur can be detected on the surface of the solution-cast film. This apparent influence of the preparation parameters on the intermolecular segregation of siloxane will be discussed in detail in Section 3.2.

We conclude that dimethylsiloxanes in P3HT segregate towards the surface of solution-cast and spin-coated P3HT films. It is emphasised that despite the low bulk concentration, the surfaces of the P3HT films are significantly covered

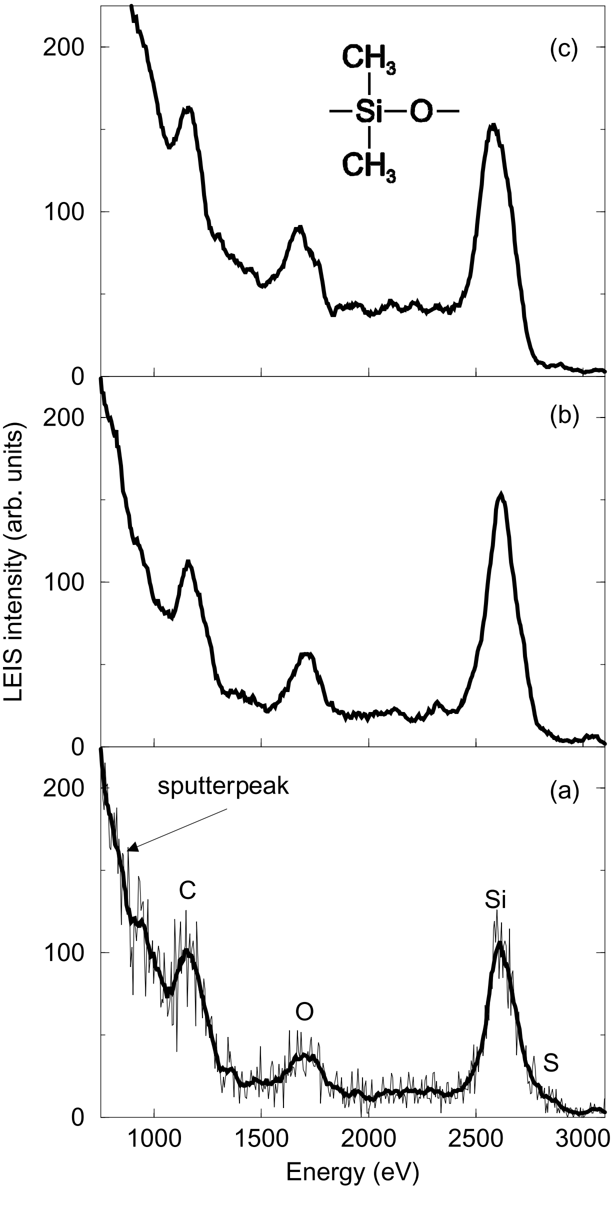

Fig. 2. LEIS spectra of (a) spin-coated P3HT film on silica/Si(100) (spinspeed 7.3×10^3 rpm, solution-concentration 7.1 mg/ml P3HT/toluene), (b) solution-cast P3HT film on silica/Si(100) (solution-concentration 4.3 mg/ml P3HT/toluene) and (c) poly(dimethylsiloxane). The spectra were recorded using 4.75 keV ^{4}He$^+$ ions and an ion dose lower than 5×10^{13} ions/cm^2.

by siloxane, which illustrates the impact of siloxane segregation on the surface composition of P3HT films, and hence on its chemical properties.

Siloxanes are frequently found as contaminants in organic materials and their presence in polymers has been reported several times [17,21,23,25,26,40–42]. The siloxanes originate from silicon grease, which is often used to connect glass tubes and reaction vessels in a synthesis set-up. McCullough et al. reported that the formation of high quality films and, therefore, the conductance of regioregular Head-To-Tail poly(alkylthiophenes) films is very sensitive to silicon grease contaminants [42]. Thus, the presence of a low bulk concentration of siloxane can greatly affect interface properties and with that the performance of organic electronic devices, like polymeric LEDs and FETs.

McCullough et al. also reported the removal of siloxanes from the bulk of as-synthesized P3HT material by means of dissolving and precipitation in hexane [42]. The 'Gardella' group occasionally reported the removal of siloxanes from polymer surfaces by means of ultrasonic extraction in hexane [17,23,25,26]. We observed that the siloxanes can be removed from the surface of spin-coated P3HT films by rinsing the films three times for about 15 min in fresh hexane at room-temperature. Other attempts to remove the siloxanes by rinsing in hexane at its boilingtemperature (69°C) or ultrasonic extraction in hexane were unsuccessful. The simple 'hexane-rinse' removes the siloxanes from the outermost surface to below the LEIS detection limit (see Fig. 3a), which is in this case below 5% of a pure DMS surface. Both LEIS and XPS show that reproducible siloxane-free P3HT surfaces can be obtained by this method (see Fig. 3). Purified spin-coated P3HT films were heated for 12 h at 350°C, which is close to the degradation temperature of 375°C for P3HT in UHV. The carbon and sulphur signals were not changed by this heating which indicates no molecular rearrangement occurred at the surface and no siloxane segregated from the bulk to the surface.

3.2. Dependence of siloxane surface density on preparation method

In order to investigate the influence of film preparation on the siloxane surface enrichment of P3HT, two series of P3HT films were prepared using solution-concentrations of 4.3 and 7.1 mg/ml P3HT/toluene, respectively and spin-speeds ranging from 0 (casting) to 15×10^3 rpm. Immediately after preparation the films were introduced into the UHV system and analysed by LEIS and XPS. Fig. 4 presents both the obtained LEIS (left column) and XPS (right column) data. The thicknesses of the solution-cast films are 1 μm (4.3 mg/ml P3HT/toluene) and 5 μm (7.1 mg/ml P3HT/toluene) and those of the spin-coated films range from 10 to 50 nm depending on concentration and spin-speed.

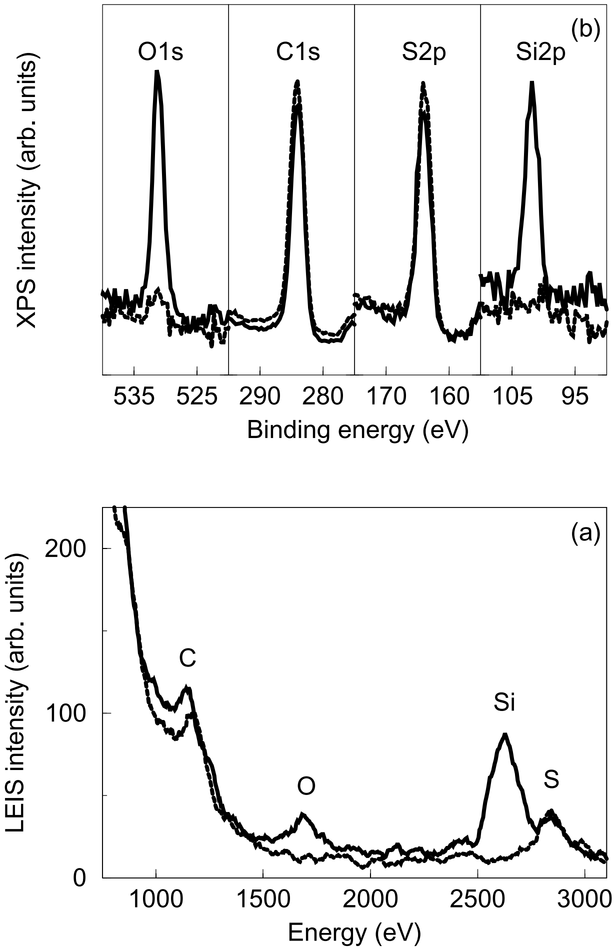

Fig. 3. LEIS (a) and XPS (b) spectra of a spin-coated P3HT film (spinspeed 4.7×10^3 rpm, solution-concentration 4.7 mg/ml P3HT/toluene) recorded before (solid lines) and after (dotted lines) rinsing in hexane at room-temperature. The LEIS and XPS measurements were performed using 4.75 keV $^4He^+$ ions and MgKα radiation, respectively.

The XPS data indicate that the silicon and oxygen atomic fractions decrease upon the use of higher spinspeeds (Ω) or solutions with lower concentrations (c), while those of carbon and sulphur increase. Also LEIS shows a decrease of the silicon and oxygen signals and an increase of the sulphur signal upon higher Ω or lower c. Hence, the siloxane surface density decreases upon the use of higher spinspeeds and less concentrated solutions. The detection of sulphur at the spin-coated films by LEIS, as well as the relatively low silicon and oxygen signals, points out that these P3HT films are only partially covered by segregated siloxanes.

The carbon LEIS signal decreases when the siloxane surface density decreases, yet one would expect it to increase considering (i) the chemical compositions of siloxane and P3HT, and (ii) the observed increase of the carbon atomic fraction by XPS. This decrease is due to screening effects (shadowing and shielding) on the LEIS signal. Atoms or molecular groups at the surface can shadow underlying atoms. Hydrogen is too small to produce a significant shadow cone, yet it can efficiently neutralise primary ions and, therefore, shield underlying species

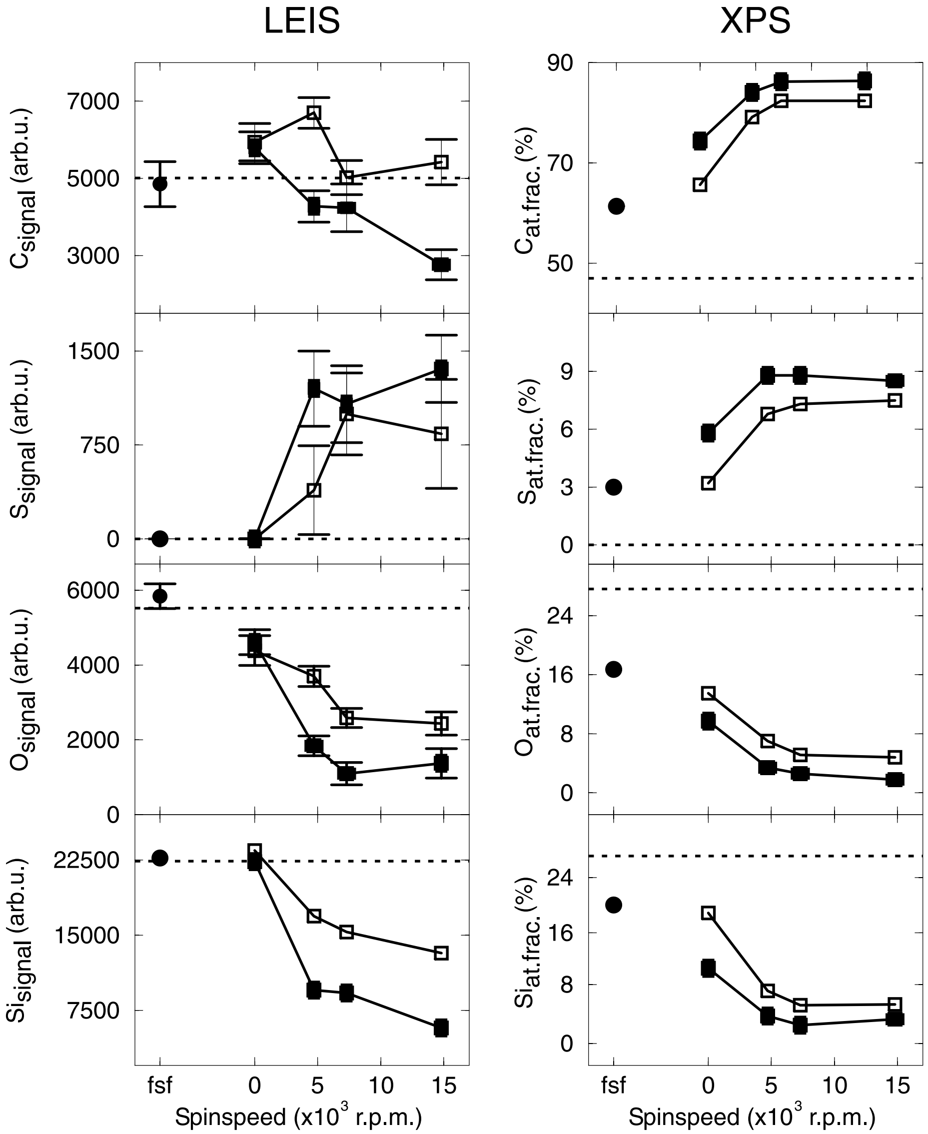

Fig. 4. Dependence of the siloxane surface enrichment on spinspeed and solution-concentration. The left and right column present respectively the LEIS signals and the from XPS data calculated atomic fractions (under assumption of a homogeneous element distribution in the surface region). The filled and open squares denote the use of solution-concentrations of respectively, 4.3 and 7.1 mg/ml P3HT/toluene. The filled circle (fsf) indicates the data of the as-synthesized free-standing P3HT film. The dashed line represents the data of pure PDMS.

[37,38]. The data suggest that P3HT-carbons are on an average more screened than siloxane-carbons, most likely due to the presence of the hexyl side-chains.

The LEIS data were quantified in terms of a surface coverage fraction, i.e. the fraction of surface-area that resembles the (reference) surface of pure PDMS. The silicon LEIS signal is the most suitable for the quantification purposes, as LEIS is much more sensitive to silicon than to carbon, oxygen and sulphur. Therefore, an estimate of the siloxane coverage fraction is provided by the ratio of the silicon LEIS signal to that of the pure PDMS reference. In Section 3.3 the validity of this quantification approach is evaluated. Fig. 5 presents the thus obtained siloxane coverage fractions as a function of the preparation parameters, spinspeed and concentration. It illustrates the impact of siloxane segregation on the outermost surfaces of P3HT films: the siloxane coverage fractions is found to range from 25% to a fully closed siloxane layer on P3HT.

To explain the dependence of the siloxane surface density on the preparation parameters we consider the following. The XPS data (Fig. 4) show that none of the prepared films is fully surface enriched by siloxane, for all observed siloxane surface densities are lower than that of the as-synthesized P3HT film. This implies that a certain factor limited the segregation of siloxane in the prepared P3HT films. No change in surface composition was recorded either upon heating to about 350°C for 1 h and 45 min or upon storage of solution-cast and spin-coated P3HT films for three months at room-temperature in a nitrogen filled glovebox. Hence, no siloxane segregation occurred anymore at

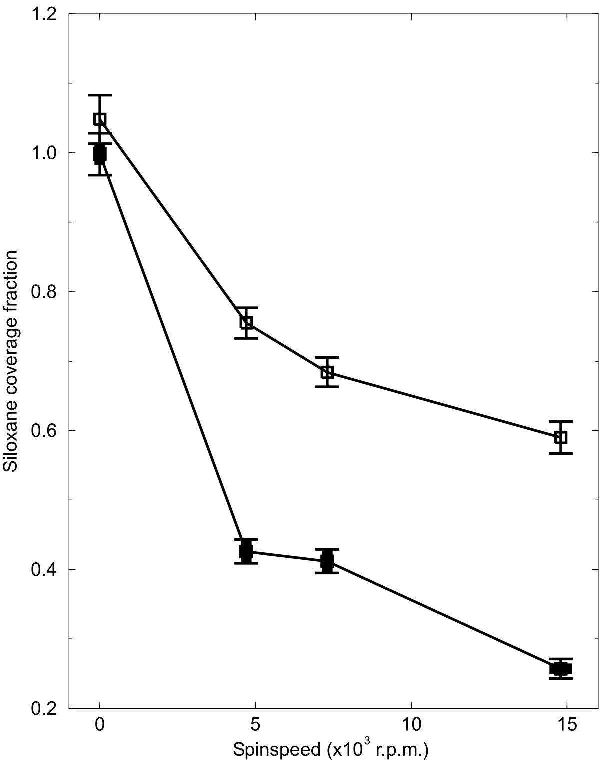

Fig. 5. Siloxane coverage fraction on top of spin-coated and solution-cast P3HT films as a function of spinspeed and solution-concentration. The filled and open squares denote the use of solution-concentrations of respectively, 4.3 and 7.1 mg/ml P3HT/toluene.

the time of analysis by LEIS and XPS and siloxane segregation was not limited by the spin-coating process, i.e. a too short dry-time with respect to the rate of segregation.

We suggest that segregation was limited by the amount of siloxane present in the films. The observed influence of preparation on siloxane surface enrichment is then explained by the thinner films prepared by higher spinspeeds and lower solution-concentrations, which results in a smaller amount of siloxane molecules available in the film to segregate to the surface. Two arguments support this. Firstly, in the spin-coated films indeed a linear dependence of both the atomic fraction of silicon (XPS) and the silicon LEIS signal is observed as a function of film thickness, i.e. as a function of the amount of siloxane. Secondly, we can simply estimate the total amount of siloxanes in the films on the basis of the bulk concentration of siloxane monomers. For a film of 30 nm thick, we then expect a maximum thickness of the segregated film of roughly 0.2 nm, which is not sufficient to cover the surface completely, but high enough to result in a significant covered fraction.

Unlike the spin-coated P3HT films, the outermost surface composition of solution-cast films does not depend on the solution-concentration. Furthermore, it resembles the topmost surface of pure PDMS (dashed line) and as-synthesized P3HT (filled circle) as displayed by the LEIS data in Fig. 4. In contrast, XPS indicates the siloxane surface enrichments of the solution-cast films do depend on the solution-concentration and are lower than that of the as-synthesized P3HT film. These observations imply that siloxanes segregate towards sub-surface layers in P3HT films, although the outermost surface is fully covered by siloxane. This suggests that the heat of mixing of siloxane in P3HT is positive (endothermic). The ‘ongoing’ segregation can also lower the free energy by diminishing concentration gradients between the siloxane surface-layer and P3HT underneath, since a steep concentration gradient imposes a free energy penalty [43].

3.3. Orientation and position of siloxane molecules at the surface

3.3.1. Preferential site of siloxane molecules at the surface

LEIS can also be used to determine whether or not siloxane molecules prefer specific orientations or sites on the P3HT surface. For this purpose, we consider the sputter-profile of a spin-coated P3HT film with a siloxane coverage fraction of 82 ± 5% (see Fig. 6). The profile was taken by means of subsequent LEIS measurements with 3 keV ^{3}He$^+$ ions. The sputter-profile can be qualitatively interpreted in terms of a compositional depth-profile, assuming a typical surface density of 1×10^{15} atoms per cm^2 and sputter-efficiency of 10%, i.e. 0.1 target atom is sputtered per incident ^{3}He$^+$ ion.

Fig. 6c displays the sulphur LEIS signals of the siloxane–P3HT surface (filled squares) and a siloxane-free P3HT surface (open squares) as a function of ion dose. These films were prepared in exactly the same manner, except for the removal of siloxane by extraction in hexane in the case of the siloxane-free P3HT film.

The sulphur signal of the siloxane-free film is prior to sputtering the highest and increases the fastest upon sputtering. The strong increase of the sulphur signals after only low ion dose indicates that the sulphur density at the outermost surfaces is considerably lower than that directly sub-surface. On the surface of the purified P3HT film the sulphur atoms are screened by easily sputtered particles; presumably parts of the hexyl side-chains and in particular hydrogen atoms. A-polar groups have generally the lowest surface energy and are hence favoured to be situated at the outermost surface. Clearly additional screening of sulphur atoms occurs when segregated siloxanes are present on the P3HT surface.

After an ion dose of 1.5×10^{16} ions/cm^2 the sulphur signal of the siloxane–P3HT surface has increased to about 80% of that of the siloxane-free P3HT film, yet a significant part of the surface is still covered by siloxane, about 60% according to the silicon and oxygen signals. This implies that siloxane molecules prefer specific sites on P3HT, such that sulphur atoms are screened by the siloxane-methyl groups. The silicon–oxygen backbones hardly screen the sulphur atoms. Most likely, the siloxane molecules prefer sites on the hexyl side-chains, which is

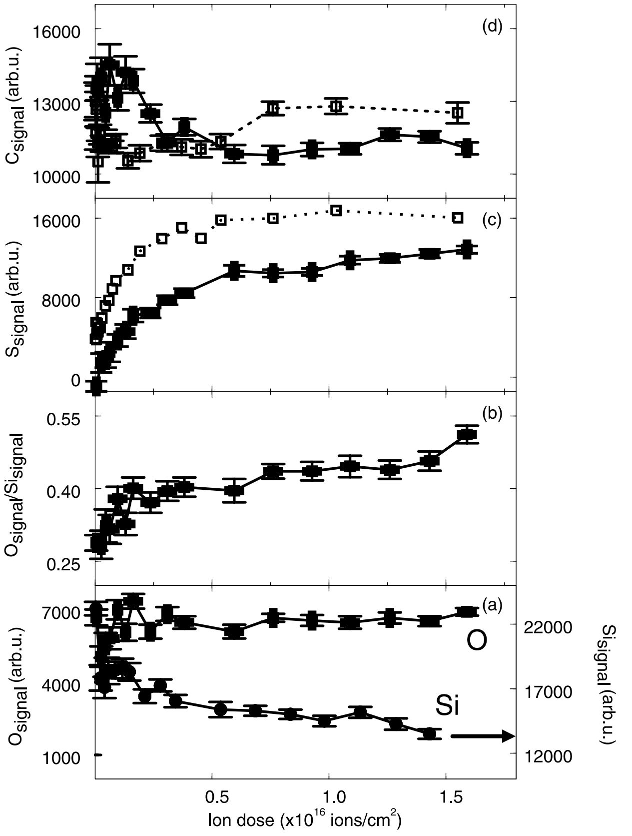

Fig. 6. Sputter-profile of a spin-coated P3HT film (spinspeed 3×10^3 rpm, coating-liquid 4.7 mg/ml P3HT/toluene) recorded by subsequent LEIS measurements using 3 keV $^3He^+$ ions. The figure shows in (a) the oxygen (filled squares) and silicon (filled circles) signals, in (b) the signal-ratio of oxygen to silicon, and in (c) and (d) the sulphur and carbon signals (filled squares), respectively as well as those obtained on the siloxane-free P3HT surface (open squares).

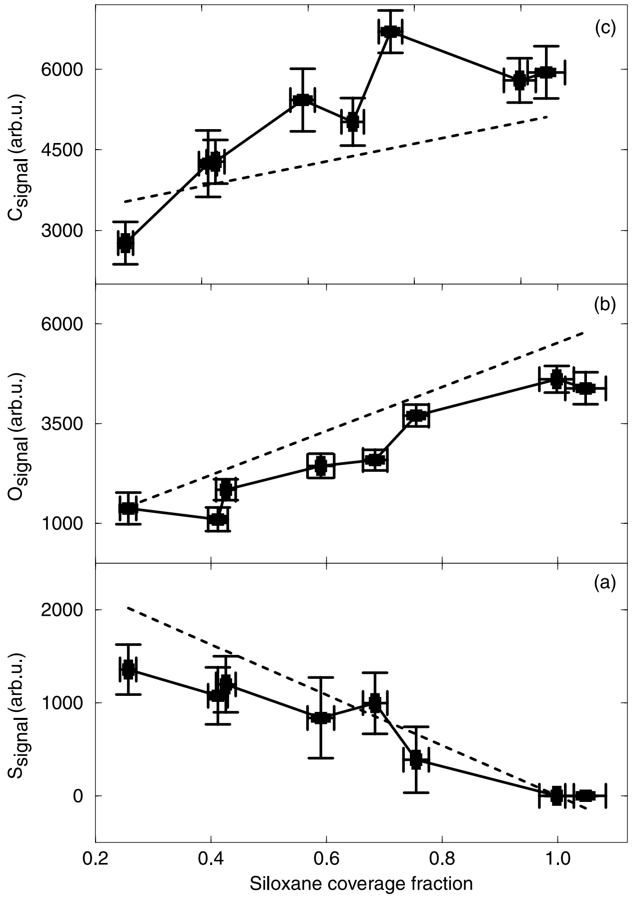

Fig. 7. Measured (solid lines) and calculated (dashed lines) LEIS signals of sulphur (a), oxygen (b) and carbon (c) as a function of the siloxane coverage fraction. These data are derived from the data depicted in Figs 4 and 5.

supported by the fact that siloxanes can be readily removed by hexane extraction.

3.3.2. Orientation of the siloxane molecules

The sputter-profile also provides information about the molecular orientation of the siloxanes on P3HT. Fig. 6a shows a gradual decrease of the silicon signal (filled circles) as a function of the ion dose, which indicates that silicon atoms are sputtered from the surface. In contrast, the oxygen signal (filled squares) is about constant, despite the sputtering of oxygen atoms. In Fig. 6b this difference in trends is more clearly illustrated by the increase of the signal-ratio of oxygen to silicon as a function of ion dose, in particular at ion doses below 6×10^{15} ions/cm^2. This indicates that the orientation of siloxane molecules is such that the silicon atoms and, therefore, the methyl groups are preferentially situated at the surface and partially screen the underlying oxygen atoms. Hence, sputtering of silicon atoms and particularly the methyl groups on the surface by ion beam irradiation reduces the screening of oxygen (and likely to a lesser extent of silicon) and raises the oxygen to silicon signal-ratio. This is consistent with the observed decrease of the carbon signal up to an ion dose of 6×10^{15} ions/cm^2 (see Fig. 6d). This is in agreement with earlier studies for siloxane polymers (including PDMS) by Hook et al., where it was suggested (based on a LEIS study with 2 keV $^3He^+$ ions), that as the topmost surface is sputtered away the siloxane oxygens become less screened, and therefore the oxygen to silicon and oxygen to carbon signal-ratios increase [22]. Our results here show that similar orientation effects occur for small siloxane molecules.

To obtain additional information concerning the orientation and position of segregated siloxane molecules on P3HT, measured LEIS signals were compared with LEIS signals calculated on the basis of the quantified siloxane surface density (derived in Section 3.2) and the reference signals measured on pure P3HT and PDMS surfaces. Fig. 7 shows as a function of coverage fraction the measured sulphur, oxygen and carbon LEIS signals (solid lines) and the calculated LEIS signals (dashed lines). The measured sulphur signals are lower than expected on the basis of the siloxane coverage, in particular at low coverage fractions (see Fig. 7a). This is consistent with the observed preferential positioning of siloxane molecules on P3HT such that the sulphur atoms are screened by the methyl groups. The

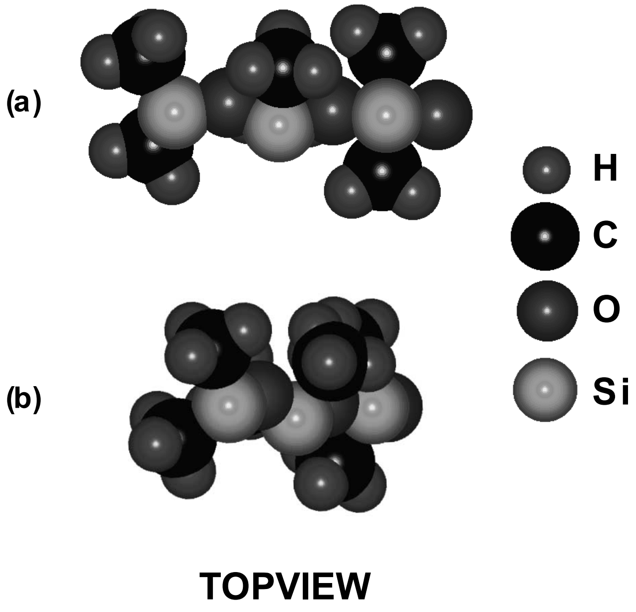

Fig. 8. Schematic illustration in topview of the out-of-surface tilting of a (short) siloxane molecule from a flat (a) to a more upright (b) orientation.

measured carbon signal is on an average higher than expected (see Fig. 7c), whereas the measured oxygen signal is lower than expected (see Fig. 7b). We suggest these deviations are due to a slight difference in orientation between siloxane molecules on P3HT and on pure PDMS. To illustrate this, Fig. 8 depicts in topview schematically the out-of-surface tilting of a (short) siloxane molecule from a flat (Fig. 8a) to a more upright (Fig. 8b) orientation, such that the methyl groups are more prominently present at the surface and the oxygen atoms are better screened. The elemental surface densities in these two orientations were compared by determination of the area per kind of atom visible to a perpendicular incident ion beam, and the presence of hydrogen was neglected. The tilt to the upright orientation leaves the silicon density unchanged, whereas the carbon and oxygen densities become 1.2 and 0.56 times the corresponding density, respectively, in the flat orientation. Hence, a slight tilt in orientation of the siloxane molecules can account for the observed deviations of the carbon and oxygen signals without changing the silicon signal. We conclude that the orientation of siloxane molecules on P3HT resembles that on pure PDMS, yet it differs slightly such that the methylgroups are more prominently present at the surface and the oxygen atoms are better screened. The orientation of the siloxane molecules on P3HT in fact depends somewhat on the coverage fraction, as can be deduced from the LEIS data in Fig. 4. The oxygen and carbon signals of a fully closed siloxane layer on top of solution-cast P3HT films differ from those found on pure PDMS, whereas on a thick siloxane layer, as found on the as-synthesized P3HT film, the signals are equal to those on pure PDMS.

3.3.3. Influence of orientation on quantification of surface coverage

In Section 3.2 the siloxane surface enrichment of P3HT films was quantified in terms of a coverage fraction which was determined by the ratio of the silicon LEIS signal of siloxane on P3HT to that of the pure PDMS reference. In general, the quantification of the siloxane coverage via the silicon LEIS signal would be affected by the observed differences in orientation. Nonetheless, the equality of the measured silicon signals of pure PDMS, the as-synthesized P3HT film and the fully-closed siloxane surfaces on solution-cast P3HT films indicates, that the silicon LEIS signal is not affected by the deviation in orientation or the preferential positioning. Therefore, it is concluded that the employed quantification method does provide a valid estimate of the siloxane coverage fraction.

4. Conclusions

The intermolecular segregation of siloxane in P3HT towards the surface was observed. The siloxane surface enrichment depends strongly on the parameters used to prepare the P3HT film the siloxane surface coverage decreases upon the use of a higher spinspeed and lower solution-concentration. This is due to the small amount of siloxanes present in these films which limit the segregation before the surface is saturated. In P3HT films with the topmost surface fully covered by siloxane, segregation of siloxane to sub-surface layers was observed. It is suggested, that this segregation lowers the free energy due to a positive heat of mixing (endothermic) of siloxane and P3HT and by decreasing concentration gradients at the siloxane–P3HT interface.

Although the number of siloxane monomers in the bulk is only 2% of the number of P3HT monomers, the siloxane coverage fraction was found to range from 25 to 100% (depending on the preparation method). These high coverage fractions illustrate the impact of a low siloxane bulk concentration — which is commonly found in polymers as an impurity — on the composition of the topmost surface. We point out that the presence of siloxanes can greatly affect surface and interface properties such as adhesion and charge injection in organic electronic devices.

Segregated siloxane molecules on P3HT prefer specific sites, likely on the hexyl side-chains, such that sulphur atoms are screened by the methylgroups from being at the outermost surface. The silicon–oxygen backbones hardly screen the sulphur atoms. The molecular orientation of siloxanes on P3HT resembles that on a pure PDMS film, yet it differs slightly such that the methylgroups are more prominently present at the surface and the oxygen atoms are better screened. This small deviation in orientation is absent when the siloxane coverage has reached saturation.

Reproducible siloxane-free surfaces of spin-coated P3HT films were obtained by the removal of siloxane via a simple rinse in hexane. Both the investigated siloxane-free and siloxane-covered P3HT surfaces are thermally stable to temperatures of about 350°C in UHV.

Finally, we wish to emphasize that although LEIS is not commonly used in the study of organic materials, the results presented in this paper on the segregation of organic molecules in a polymer show quantitative segregation studies and studies on the orientation of molecular groups at the surface are possible. This information is not easily obtained from other techniques.

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