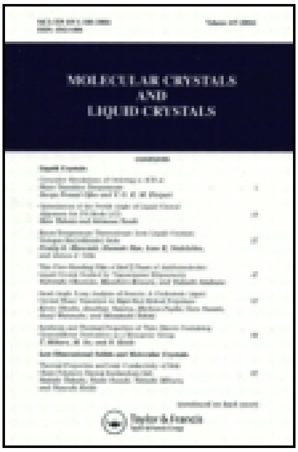

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Surface Species of Poly(p-Phenylene Vinylene) and Their Effects on Calcium Interface Formation

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Version of record first published: 04 Oct 2006.

To cite this article: B. R. Hsieh , E. Ettedgui , K. T. Park & Y. Gao (1994): The Surface Species of Poly(p-Phenylene Vinylene) and Their Effects on Calcium Interface Formation, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 256:1, 71-78

To link to this article: http://dx.doi.org/10.1080/10587259408039233

Mol. Cryst. Liq. Cryst. 1994, Vol. 256, pp. 71–78
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THE SURFACE SPECIES OF POLY(p-PHENYLENE VINYLENE) AND THEIR EFFECTS ON CALCIUM INTERFACE FORMATION

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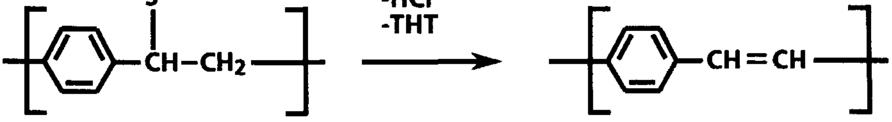
Abstract X-ray photoemission spectroscopy (XPS) was used to investigate the surface species of poly(phenylene vinylene) (PPV). PPV samples with 1% S and 5-10% O impurities were obtained whenever the corresponding sulfonium precursor polymers were subjected to XPS scans prior to thermal conversion. Relatively "clean" PPV surfaces with 4-5% oxygen atoms as the only detectable impurities were obtained by performing the thermal conversion in an argon circulating oven or in ultra high vacuum at 320°C, without prior XPS scan. Therefore the S impurities were resulted from x-ray induced chemical reactions which might involve the formation of sulfur ylides. By resolving the O 1s peak, four types of oxygen species were identified, namely carbonyl (C=<u>O</u>), hydroxy (C-<u>O</u>H), ether (C-<u>O</u>-C) and the carboxylic groups (H<u>O</u>-C=O). The oxygen groups reacted with Ca to form CaO. A reversed surface band bending was found for the S containing PPVs with respect to that for the S free PPVs during the Ca interface formation. Our overall results suggest that the barrier height at metal/PPV interface is highly sensitive to the surface preparation and relatively insensitive to the work function of the metals.

INTRODUCTION

Prompted by the fact that the efficiency of electroluminescence for poly(phenylene vinylene) (PPV) based light-emitting diodes (LED) is highly dependent on the type of metal cathodes[1-4], we have initiated the investigation of interface formation of metal with PPVs [5-7]. By understanding the nature of the metal/PPV interface, we hope to be able to address issues related to the stability and the efficiency of PPV based LEDs as well as other organic opto-electronic devices.

The first step to a meaningful investigation of PPV/metal interfaces is to identify the surface compositions of PPV. In this paper, we report the x-ray photoelectron spectroscopy (XPS) results on the surface compositions of PPV films derived from thermal conversion of a sulfonium precursor polymer as shown below [8,9]. The earlier XPS data for the sulfonium derived PPV



indicated the presence of impurities such as oxygen (2.5%) and small amounts of sulfur and silicon (both less than 1%) [10]. Two of the objectives of this surface investigation are to minimize the surface impurities and to learn their effects on metal interface formation. A "clean" surface is highly desirable because it can simplify the chemistry of interface formation and can thus lead to a better understanding.

EXPERIMENTAL

A detailed description of the XPS and ultra-high vacuum (UHV) systems used in this study has been presented elsewhere [11]. The energy resolution of the XPS spectrometer was 1.2 eV, resulting from the convolution of the natural width of 0.68 eV of the MgKα line and the resolution of 1.0 eV chosen for the hemispherical energy analyzer. The thin PPV films were prepared by solution cast from an aqueous solution of a tetrahydrothiophenium precursor polymer shown above [8,9] or spin cast from a methanol solution of the same polymer on a flat Al substrate, followed by in situ thermal conversion in the UHV system or ex situ in an argon circulating oven at 200-320°C. The thicknesses of the solution and the spin cast samples were about 1000 and 200 Å respectively. The deposition of Ca or Al was accomplished by evaporating it from a resistively heated tungsten boat with an average rate of 1 Å/min. The thickness of the deposited layers were monitored by a quartz crystal thickness monitor, and this quantity was used as the nominal thickness of the metal overlayer. During the deposition, the PPV film was kept at room temperature. XPS spectra were recorded at preselected coverage. The time for the evaporation and data acquisition is about 1.5 h for each coverage.

RESULTS AND DISCUSSION

Table 1 summarizes the the surface compositions and the thermal conversion conditions for the first set of six samples (samples 1-6). The XPS spectra were taken before and after thermal conversion for samples 1-4. Samples 5 and 6 are the precursor polymer films. As can be seen from Table 1, there is a wide range of %O of 5.3-22% for the as cast precursor polymers. Although samples with low %O of 5-6%, such as sample 3 and 4, were obtained on occasions, a %O of 13% is more representative for the precursor polymer. As expected, the S and Cl percents were about the same. Although Cl could be completely eliminated by heating at 150-200°C, about 1% of S reminded after conversion at 320°C. (The nature of the residual S will be discuss later.)

We were able to achieve relatively "clean" PPV samples that are low in %O and free from sulfur impurities, as listed in Table 2. The surface compositions for samples prepared under argon (samples 7 and 8) or in UHV (samples 9-11) at 320°C are essentially identical. Thermal conversion under argon at 250°C gave sample 12a which was further heated in UHV at 320°C to give sample 12b. The second heating reduces %O from 11.5 to 5.0. By converting at 320°C, samples 7-11 and 12b all show similar surface compositions indicating a high degree of reproducibility associated with our conversion processes. Sample 13a which is a six-week aged sample 12a shows an increased in %O to 14.7 indicating the interaction of PPV surface with the ambient environment, especially with O_2 and H_2O. The %O is reduced to 10.3 after heating at 320°C/2h. We found that prolong heating at 320°C did not further reduce the %O; higher temperature may be needed to further reduce the %O in all cases. For the second set of

Table 1. Surface atomic percents for the Sulfonium polymer films and the corresponding PPV films[a]

sample no.	conditions for consersion	%C	%O	%S	%Cl
1[b]		(82.6)	(13.0)	(2.6)	(1.8)
	150°C/1h in UHV	85.8	12.0	1.2	1.0
	200°C/2h in UHV	89.6	9.5	0.8	0
2[b]		(75.0)	(22.0)	(1.5)	(1.5)
	200°C/2h in UHV	82.0	17.0	1.0	0
3[c]		(89.8)	(6.0)	(2.1)	(2.2)
	250°C/2h in UHV	94.8	4.1	1.1	0
4[c]		(91.0)	(5.3)	(2.3)	(1.2)
	320°C/2h in UHV	95.0	4.0	1.0	0
5[c]		(83.1)	(13.2)	(2.0)	(1.7)
6[c]		(84.0)	(13.0)	(1.6)	(1.4)

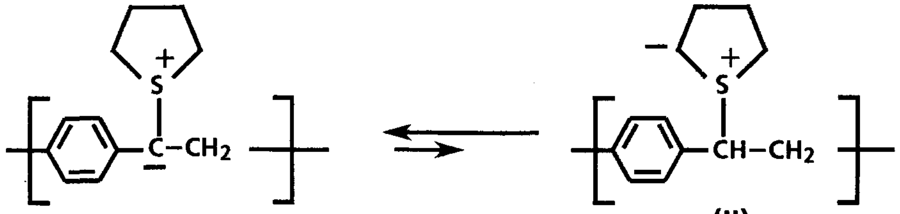
a. Data for the as cast precursor polymer samples are given in parentheses.
b. Cast from water solution.
c. Cast from methanol solution.

Table 2. Conversion conditons and surface atomic percents of PPV films[a]

sample no.	conditions for consersion	%C	%O
7	320°C/2h under argon	94.0	6.0
8	320°C/2h under argon	95.0	5.0
9	320°C/2h in UHV	94.9	5.1
10	320°C/2h in UHV	94.7	5.3
11	320°C/2h in UHV	94.3	5.7
12a	250°C/2h under argon	88.5	11.5
12b	320°C/2h in UHV	95.0	5.0
13a	sample 12 a 6 week later	85.3	14.7
13b	320°C/2h in UHV	89.7	10.3

a. Data given in atomic percent and samples were prepared by spin cast using a methanol solution of the precursor polymer.

samples (shown in Table 2), no XPS scans were taken for the corresponding precursor polymer films prior to thermal conversion. In other words, XPS data were recorded after thermal conversion had been performed. This is in contrast to the first set of sulfur containing samples (samples 1-6 shown in Table 1) where XPS scans were taken before and then after the thermal conversion. We therefore conclude that the sulfur impurities present in the first set of samples were resulted from x-ray induced chemical reactions. Radiation of a sulfonuim chloride group may generate two types of sulfonium ylides (I) and (II) [12] shown below (the corresponding ylene resonance forms not shown). Type (I) ylide is likely to be the major species because deprotonation of a benzylic proton is easier than an aliphatic proton. In addition, ylide (I) is more stable than ylide (II) and may even survive after thermal treatment. Both ylides may undergoes various rearrangements to give sulfide products [13]. X-ray may also induce neucleophlic attack of the sulfonium groups by water, methanol and hydroxy groups present in the polymer to give the ring opened and the crosslinked products containing sulfide groups. Therefore, the sulfur impurities may include sulfonium ylides and various sulfide groups.



(I) (II)

The XPS %O of 5-13% for PPV is not in accord with the bulk %O of < 1% determined by elemental analysis [14]. The high %O on the PPV surface is likely due to surface segregated oxygen impurities. Surface oxygen segregation is a well known phenomena in polymer systems [15] and can be due to factors such as polymer chain ends, oxygen defects and surface contamination and surface oxidation . In order to identify the oxygen species, decomposition of O 1s core level peaks was performed for selected samples. As shown in Fig. 1, the broad raw oxygen peaks of samples 12a and 12b can be fitted very nicely with three Gaussian peak components with similar widthes. Poor fits were obtained from two-component decomposition. Table 3 summarized the peak positions and the percentages for several samples. The data are highly consistent among the samples showing three peak components at about 531.0, 532.0 and 533.0 eV. We respectively assigned these to carbonyl oxygen ($C=\underline{O}$), hydroxy/ether oxygen ($C\text{-}\underline{O}H$/ $C\text{-}\underline{O}\text{-}C$) and the carboxylic acid groups ($H\underline{O}\text{-}C=O$) according to the data of Lopes et al [16]. In all cases, component 2, which corresponds to the hydroxy and ether groups, is the dominant component. This is understandable because the presence of hydroxy groups in the surfonium precursor polymer is well known [17] and they can attack the sulfonium groups to form ether crosslinkages. This is likely to be the process associated with the instability of the aqueous sulfonium precursor polymer solutions which gel up after prolong standing [18]. Gelation takes place rapidly within one to two weeks for the methanol precursor polymer solutions [18]. This is due to the attack of sulfonium groups by methanol to form methoxy type ether groups and the crosslinking through the hydroxy groups on the precursor polymer chains. As shown in Fig. 1, the decrease in the second component upon heating at 320°C may be due to dehydration through thermal elimination of the hydroxy groups and thermal oxidation of the hydroxy groups to ketone groups. Such thermal oxidation can be reduced or avoided by performing the conversion under reduce atmosphere such as hydrogen [19]. The presence of oxygen functionalities can also be detected by the analysis of the C 1s peak. For example, the C 1s peak of sample 7 was resolved into three components with binding energies of 284.5, 285.6 and 287.4 eV, which can be assigned to $\underline{C}\text{-}C$, $\underline{C}\text{-}O$ and $\underline{C}=O$ respectively [16].

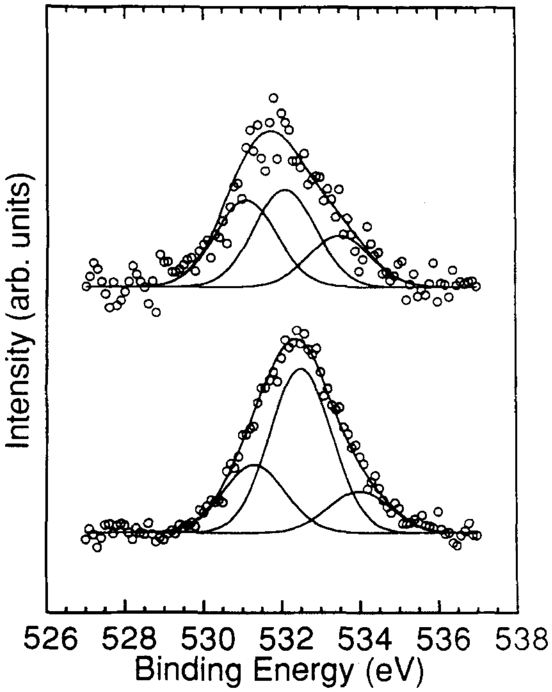


Fig. 1. Resolved O 1s EDCs for samples 12a (bottom) and 12b (top).

Table 3. XPS peak positions and area percentages of resolved oxygen components for selected PPV samples

sample no.	component 1		component 2		component 3	
	position (eV)	area %	position eV	area %	position eV	area %
7	531.1	18.5	532.0	63.0	533.6	18.5
8	531.1	26.3	532.2	53.5	533.8	20.2
12a	531.3	24.8	532.5	60.0	534.0	15.2
12b	531.0	38.9	532.1	43.6	533.5	17.5
13a	531.6	6.4	532.7	78.2	534.2	15.4
13b	531.5	27.0	532.6	53.1	533.7	19.9
peak assingment*	C=O & O-C=O 532.2*		C-OH & C-O-C 532.8*		O=C-O 533.7*	

* reported values from ref. 16.

We reported delayed surface band bending during the Ca/PPV interface formation for sample 2 where the band bending was signified by a sudden C 1s peak shift of 0.4 eV towards lower binding energy at 15 Å of Ca deposition [6]. This delay has been attributed to the screening effect of the surface impurities which retard the formation of metallic Ca and its interaction with PPV itself [6]. As shown in the left part of Fig. 2, we have reproduced the result for sample 3, even though it has a much lower %O that sample 2. The peak positions of C 1s EDCs remain almost unchanged at about 284.3 eV up to 8 Å of Ca deposition and then shift toward a lower binding energy of 283.8 eV at 15 Å of Ca. Surprisingly, a reverse direction of peak movement to higher binding energies was found for the sulfur free PPV samples. As exemplified in the right part of Fig. 2 for sample 12b, the C 1s peaks stay at about 284.2 eV till 15 Å of Ca deposition. This is followed by a peak shift of +0.4 eV to 284.6 eV at 30 Å of Ca coverage. We have been able to obtain reproducible and distinctive results as described above for both types of PPV. This clearly indicates that charging effect was negligible during our XPS investigation.

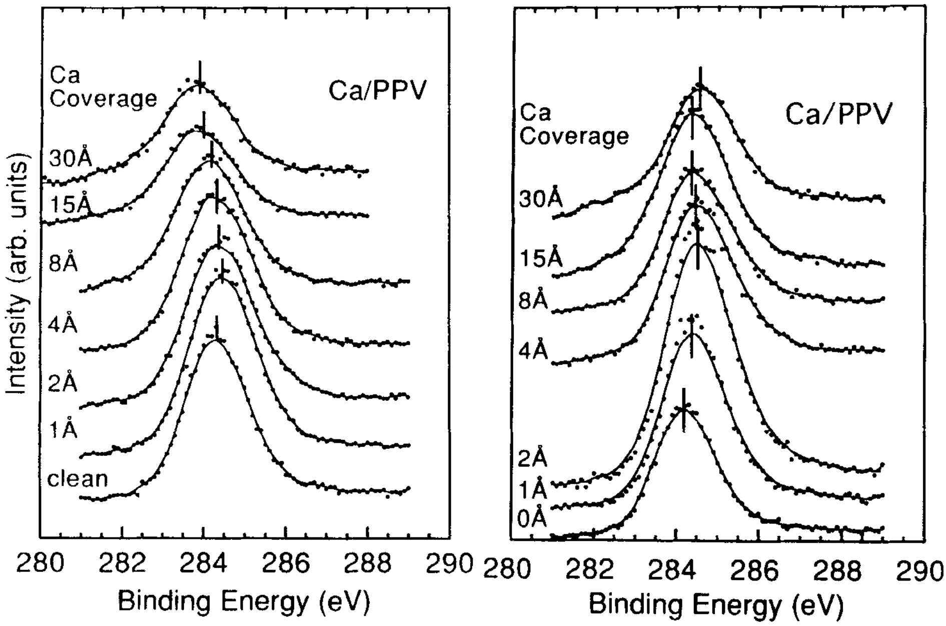


Fig. 2 The C 1s core level EDCs for sample 12a (left) and sample 12b (right) at various Ca coverages.

We interpret the above results using the qualitative energy diagram shown in Fig. 3. We assume that the valance and the conduction bands and the C 1s core level of PPV have a slight band bending initially with Fermi level situated close to the valance band. Metal induced band bending takes place upon the establishment of metallic Ca over layer at 15-30 Å on the surface of PPV. The direction of band bending is dictated by the surface species of PPV. The sulfur containing surface induces an upward band bending and thus reduces the C 1s binding energy accordingly. On the contrary, Ca induces an downward band

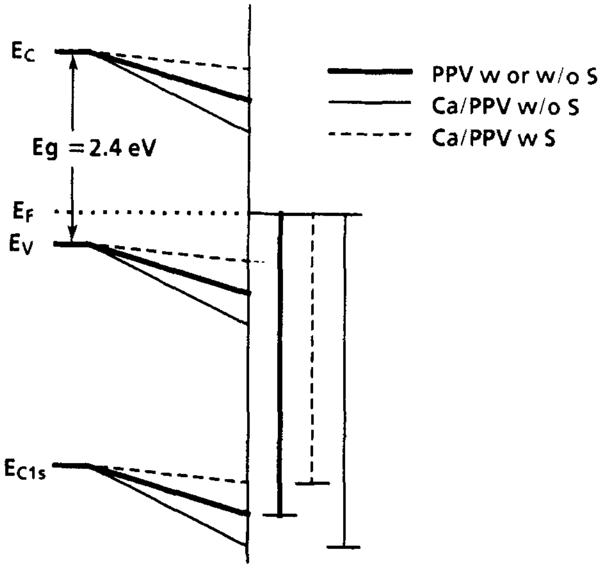


Fig. 3 Proposed energy diagrams showing different directions of Ca induced band bending for S free and S containing PPV samples.

bending for the sulfur free sample to give a higher C 1s binding energy.

In summary, Ca reacts immediately with the surface oxygen impurities to form CaO. As a result, the surface impurities delay both the formation of metallic Ca and the metal induced surface band bending. It is likely that the thickness of the metal oxide layer is proportional to the concentration of the surface impurities. Therefore, it is highly desirable to minimize the surface impurities in order to minimize the barrier heights and to improve injection efficiency. The fact that the direction of the surface band bending is highly dependence on the type of surface impurities suggest that proper surface treatment may provide a mean of modifying the barrier heights. Our results so far [5-7] suggest that the barrier height at metal/PPV interface is highly sensitive to the surface preparation and relatively insensitive to the work function of the metals. This is in agreement with the understanding in metal-semiconductor interface formation where barrier heights are often determined by the surface preparation of the semiconductors rather than the work function of the metals [20].

Acknowledgements

This work was supported in part by the National Science Foundation (Grant DMR 9303019).

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