

A study of poly(*p*-phenylenevinylene) and its derivatives using x-ray photoelectron spectroscopy

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Poly(*p*-phenylenevinylene) and its derivatives (DP-PPV and labeled R-7) were carefully studied using x-ray photoelectron spectroscopy. The C 1s peaks taken from spin-coated thin films of these materials were fitted with the consideration of the bonding state differences ($-C=CH$ and $C=C-$, etc). The intensity of these C 1s peaks agrees well with the value estimated from the bonding state consideration. © 1997 American Institute of Physics. [S0021-8979(97)05721-6]

I. INTRODUCTION

Conjugated polymers have attracted much interest in the last few years in applied science and technology for various possible application in the light emitting diodes (LEDs) and molecular electronic devices.¹⁻⁴ Despite recent intensive studies, the detailed mechanism of conduction in these polymers has been puzzling because a charge transfer between the dopant and the conjugated polymers appears as polaron or bipolaron states, whose detailed properties are still under discussion.⁵ The role of the chemical or electrochemical doping of these conjugated polymers for improving the conductivity has also been studied.⁶ Conducting polymers with extensive electron delocalization are known to be semiconductors with a relatively small band gap.⁷ Regarding the actual device fabrication, conducting and semiconducting polymers are one of the more attractive alternatives due to their processability and low cost. In addition, the organic semiconducting polymers allow one to tailor the properties of the optoelectronic devices with molecular design. However, problems of poor stability of these polymers in ambient operating conditions, which are related to the high ionization potential, must be overcome for real application. Various side group substitutions have been tried for these polymers in an attempt to enhance the stability and processability as well as electrical properties.⁸⁻¹⁰

Poly(*p*-phenylenevinylene) (PPV), which is synthesized mostly via precursor route, is a prototype luminescent polymer which shows very strong photoluminescence as well as electroluminescence. It also exhibits good physical and chemical properties for practical use such as improved stability in air. It can also be obtained in the form of tough, flexible and dense films by the simple solution casting process.^{11,12} The band gap of this material is known to be

about 2.4–3.0 eV, which was confirmed by photoluminescence measurement.¹³ The derivatives of PPV (DP-PPV and labeled R-7) show either better processability or improved electrical or chemical properties. The sample labeled R-7 is also luminescent although its chemical structure is quite different from those of PPV and DP-PPV. As shown in Fig. 1, the sample labeled R-7 has two different oxygen bonding states which will be discussed in more detail in Sec. III.

Recent photoemission studies of these materials have been focused on the effect of metal overlayers, the electrodes for LED. However, it is not easy to obtain detailed and reliable information on this metal-semiconductor interface formation process without firm baseline information of the polymers themselves.^{14,15} Konstadinidis *et al.*¹⁶ has measured the C 1s core level spectra for PPV and its derivative but their samples appear to have an appreciable amount of C–O impurity bond. The peak fitting process of the core level data obtained by Maria *et al.*¹⁷ has no physical ground making it difficult to draw a firm conclusion. In order to clarify these issues we performed an accurate and systematic study of x-ray photoemission spectroscopy (XPS) core level spectra of PPV and its derivatives. The C 1s core level spectra and the valence band spectra of PPV, DP-PPV, and labeled R-7 were obtained. The core level peaks were fitted according to the bonding state of carbon species. These spectra with the fitted results can be used as reference spectra although the changes in these spectra upon the deposition of metal layers on this would be small.

II. EXPERIMENT

All the samples used in this experiment were spin-coated from 1 wt % solutions. The solvents were chloroform(R-7), methanol(PPV) and toluene(DP-PPV). The spin casting was performed at 2000 rpm for 1 min. After the films were formed, PPV and DP-PPV were converted in flowing nitrogen environment for 2 h at 250 °C. The R-7 sample needs no

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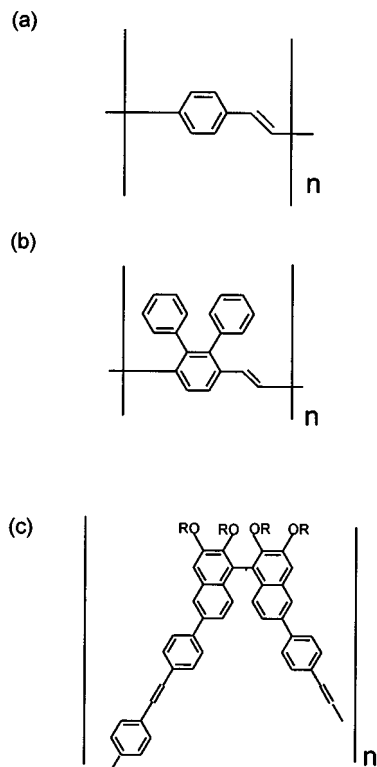


FIG. 1. The chemical structure of PPV and its derivatives. (a) PPV, (b) DP-PPV, and (c) labeled R-7, RO means $\text{CH}_3(\text{CH}_2)_5\text{O}$.

conversion step.¹⁸ More details of the synthesis of PPV can be found elsewhere.¹⁹ The substrate used in this experiment was an Au coated Si wafer on which the polymer overlayer was spin coated. We measured the photoelectron spectra at

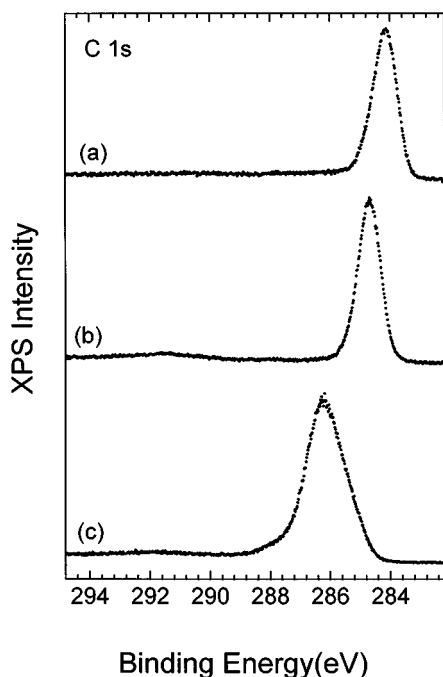


FIG. 2. C 1s core level spectra of (a) PPV, (b) DP-PPV, and (c) labeled R-7 with monochromatized x-ray source.

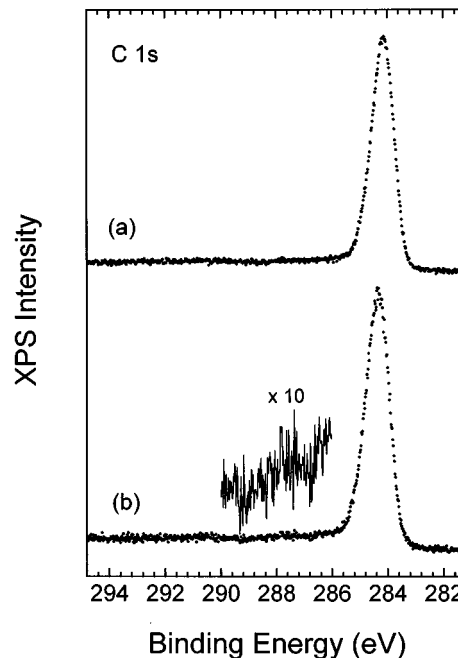


FIG. 3. C 1s core level spectra of DP-PPV with monochromatized x-ray source. The take-off angles are (a) 0° and (b) 55° from the surface normal.

room temperature using a VG ESCALAB 220 system. This system was equipped with a concentric hemispherical energy analyzer with fixed transmission mode. The pass energy was to 15 eV for C 1s core level spectra. The base pressure of the analysis chamber was maintained to be lower than 1×10^{-10} Torr. The pressure rise due to the sample was almost negligible. Throughout the experiment, monochromatic radiation from an Al K_α emission was used. At the normal emission spectrum, we could observe the substrate Au $4f_{7/2}$ peak, whose position was used to estimate the correct binding energy of the core level. We obtained the valence band spectra at the takeoff angle of 55° . To avoid the possible degradation of the polymers by the visible light, all the experiment had been performed in the dark room.

III. RESULTS AND DISCUSSION

The chemical structures of polymers used in this study are shown in Fig. 1. Although each sample has distinct structures, it is mainly made of linear chains of phenylene group and vinylene group arrays. In the structure of R-7, $-\text{RO}$ represents the $\text{CH}_3(\text{CH}_2)_5\text{O}$ functional group. From Fig. 1(c) one can see that there are two different C–O bonding states in the unit cell of R-7, which will be discussed later.

Figure 2 shows the C 1s core level spectra of the three samples. These spectra were normalized so that the peak heights are the same. The binding energy of the C 1s peak shifts toward the higher binding energy from PPV to R-7. As we will show later, the core level shift referenced to the PPV peak is 0.5 eV and 2.05 eV for DP-PPV and R-7, respectively. The observed shift may be explained by the correlation of the conduction band electrons or the work function change. The main peak of each C 1s core level spectrum originates from the aromatic and the aliphatic part of the unit

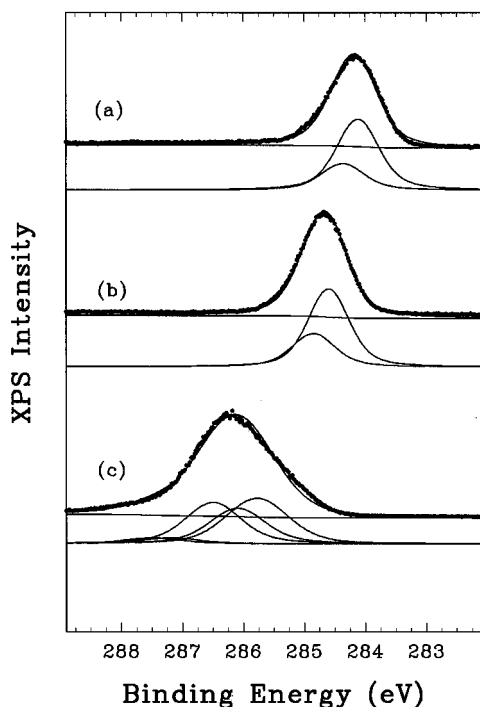


FIG. 4. C 1s core level spectra of (a) PPV, (b) DP-PPV, and (c) labeled R-7. The dots are experimental values and the solid lines represent the results of peak fitting.

cell. There are also broad peaks at higher binding energy relative to the main peak. These are the $\pi-\pi^*$ shake-up structure (6.5 eV to the higher binding energy) originating from the phenylene and vinylene groups of PPV and their derivatives.^{20,21}

Figure 3 shows C 1s core level spectra of DP-PPV taken at two different takeoff angles (normal and $\theta=55^\circ$). The fact that these spectra are almost identical suggests that the contamination at the surface, which should be more visible in the spectra taken at higher emission angle, is negligible. The peak located at about 288 eV binding energy [Fig. 3(b), inset] in the spectrum taken at a 55° takeoff angle corresponds to C 1s from the carbonyl group, which is barely visible even in the tenfold expanded spectra. The fact that this peak

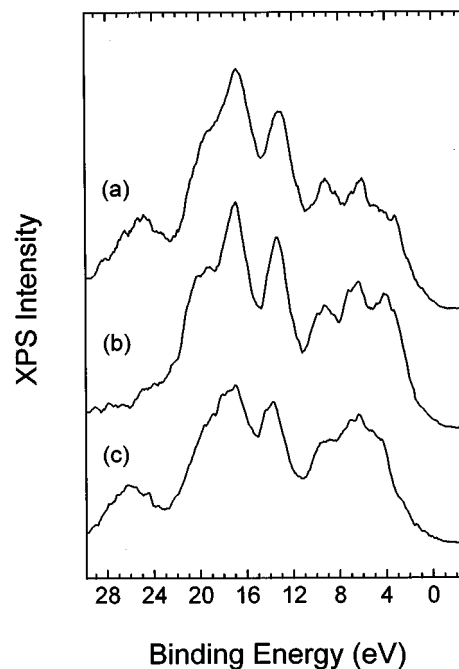


FIG. 5. Valence band spectra of (a) PPV, (b) DP-PPV and (c) R-7 with nonmonochromatized x-ray source.

is not observable in the spectrum taken at normal emission indicates that slight carbonyl contamination is limited in the near surface region.

The full width at half maximum (FWHM) of C 1s peaks is about 1–1.5 eV in our data at the pass energy of 15 eV. We did curve-fitting to the spectra using Doniac–Šunjic functions, which were broadened with a Gaussian to account for the instrumental broadening. Two criteria for distinguishing different carbon species are conceivable. In one, we may assume that the difference in hybridization (aromatic and aliphatic character) would result in different C 1s binding energies. For DP-PPV, the number of carbon atoms in the phenyl and vinylene groups are 18 and two, respectively. According to this, the intensity ratio expected is 9:1. On the other hand, if we assume that the difference in bonding states ($-\text{C}=\text{CH}$ and $\text{C}=\text{C}-$) is the origin of the binding energy

TABLE I. Fitting parameters for C 1s core level of PPV, DP-PPV, and labeled R-7. The intensity of peak A ($\text{C}=\text{C}-$) has been normalized to 1.

Sample	Sign	Bonding state	$E_{\text{bind}}(\text{eV})^a$	FWHM(eV)	Intensity	Exp. Int. ^b	Cal. Int. ^c
PPV	A	$\text{C}=\text{C}$	284.35	0.65	0.06	1.0	1.0
	B	$-\text{C}=\text{CH}$	284.1	0.64	0.17	2.83	3.0
DP-PPV	A	$\text{C}=\text{C}-$	284.85	0.65	0.21	1.0	1.0
	B	$-\text{C}=\text{CH}$	284.6	0.64	0.476	2.38	2.33
R-7	A	$\text{C}=\text{C}-$	286.05	0.64	0.29	1.0	1.0
	B	$-\text{C}=\text{CH}$	285.8	0.65	0.50	1.721	1.714
	C	$-(\text{CH}_2)_4\text{CH}_3$	286.5	0.65	0.41	1.41	1.428
	D	$-\text{C}-\text{O}-$	287.0	0.66	0.085	0.293	0.286
	E	$-\text{O}-\text{C}=\text{C}$	287.3	0.66	0.082	0.283	0.286

^a E_{bind} is binding energy referenced to the Fermi level.

^bExp. Int. is the relative intensity of each peak.

^cCal.Int. is the relative intensity calculated with the assumption of the different bonding states.

difference, the intensity ratio of two bonding states in DP-PPV should be 2.33:1. Experimental value of the ratio obtained by fitting the C 1s core level peak is 2.38:1 for DP-PPV. This result indicates that in DP-PPV, the curve fitting of this C 1s spectrum should be done based on the difference in the nature of the bonding state rather than on the difference in hybridization. We applied the same procedure to the C 1s peaks of PPV and R-7. The results of the peak fitting are shown in Fig. 4. While the C 1s peak of PPV was decomposed using the same bonding state assumption ($-\text{C}=\text{CH}$ and $\text{C}=\text{C}-$) as that of DP-PPV, the R-7 requires five different bonding states due to the two additional different carbon-oxygen bonding states, as shown in Fig. 1(c). Five different carbon bonding states used in the fitting are $-\text{O}-\text{C}=\text{C}$, $\text{CH}_3(\text{CH}_2)_4$, $-\text{C}-\text{O}-$, $-\text{C}=\text{CH}$ and $\text{C}=\text{C}-$. The results of fitting, summarized in Table I, indicate that the calculated intensities are in good agreement with the experimental values. The binding energies of the oxygen containing species [$-\text{O}-\text{C}=\text{C}$ and $-\text{C}-\text{O}-$] are 1.25 and 0.95 eV larger than that of the main ($\text{C}=\text{C}-$) bond, respectively. These data can serve as the baseline for study of the effect of the overlayer metals on the carbon signals of different species.

The valence band spectra of the three polymers are shown in Fig. 5. All the samples show several narrow photoionization peaks beginning at 4 eV below the Fermi level. According to the theoretical calculation of Maria *et al.*¹⁷, we may assign the origin of these peaks between 3 and 10 eV to the $\pi-\pi^*$ bonding, while the peaks between 10 and 30 eV are assigned to the σ bonding. In the case of PPV and R-7, we could see a broad peak between 24 eV and 27 eV below E_F , which are thought to come from oxygen, since we could observe the existence of a small amount of oxygen peak in the survey spectrum of PPV. Oxygen concentration in PPV was estimated to be about 3.0%. For DP-PPV, no signature of oxygen was observed in both valence and core level spectra.

IV. CONCLUSION

We have measured the C 1s core level spectra of PPV and its derivatives, DP-PPV and R-7. The assignment of the local carbon site in the core level spectrum based on the chemical bonding states yielded a good agreement in relative

intensity of C 1s peaks with the experimental values. The bonding site obtained here can be used to track the effects of the metal overlayers on different species of carbon atoms in each polymer. The valence band spectra taken with XPS showed good agreement with the reported assignment of theoretical calculations.

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