# UV Photoelectron Spectroscopy of Substituted Polyacetylenes

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Ionization threshold energies of 26 substituted polyacetylenes were determined by ultraviolet photoelectron spectroscopy. Examination of the data obtained, along with data for other polymers, and the energy of the lowest energy electronic excitation revealed that the threshold energies correspond to the photoemission from the highest occupied orbitals in the $\pi$-conjugated main chains. For the majority of the polymers, the main origin of the significant variation of threshold energy and electronic excitation energy is ascribed to the change of the degree of $\pi$-conjugation due to steric hindrance of substituents. Calculations with Hückel theory gave semiquantitative agreement with the observed results. Polymers with Cl substituents at the main chain also showed a large inductive effect by the electron-withdrawing Cl atom. The HOMO of these polymers was found to be derived from the $\pi$-conjugated main chain.

## I. Introduction

Due to their unique electronic and electric properties, the study of $\pi$-conjugated polymers has recently been the focus of numerous investigations. Polyacetylene is one of the representative polymers of this type and shows metallic conductivity upon n- and p-type doping.[1] Although its practical use is limited due to its instability in air, when the hydrogen atoms in polyacetylene are substituted by various functional groups, the resultant polymers (substituted polyacetylenes) generally become stable in air.[2,3] Moreover, metallic conductivity by doping is not anticipated for these polymers because the pristine polymers are generally insulators. However, they have moderately conjugated $\pi$ electron systems and exhibit various functions such as photoconductivity.[3,4] Thus the elucidation of their electronic structures is interesting, but there have been no systematic studies except for the measurements of UV absorption spectra.[2,3] The excitation energies of the UV absorption significantly varies over a range 2.3−5.0 eV, but the origin of the variation has not yet been well clarified.

In this paper we report on the UV photoelectron spectroscopy (UPS) of substituted polyacetylenes. UPS is a powerful tool for examination of the occupied electronic structure of materials including polymers.[5,6] The observed results in conjunction with the results of UV−visible absorption have provided a unified picture of the electronic structures of substituted polyacetylenes.

## II. Experimental Section

The polymer samples were synthesized as reported in previous publications.[2,3] Their structures are shown in Figure 1. The samples used in the UPS measurements were prepared on a copper disk of 12 mm diameter by spin coating of a drop of polymer solution in tetrahydrofuran. For sample **5**, toluene was used as the solvent. The sample was placed at the center of a spherical collector coated inside with gold located in a $10^{-3}$ Pa sample chamber. Two types of discharge lamps, operated by microwave of 2450 MHz, were used as the light source. One

was a mercury lamp with a quartz window with the maximum energy of a photon of 6.7 eV (emission line at 184.9 nm).[7] The other was a xenon resonance lamp with a LiF window, which emits almost monochromatic light of 8.41 eV. The photoelectrons emitted by the light were detected as the photocurrent $I_{ph}$. Their kinetic energy distribution was analyzed by applying a variable retarding field $V_r$ between the sample and the collector by the ac modulation technique,[8,9] with a modulation voltage of 0.2 V peak to peak.

An example of the observed spectra is shown in Figure 2, which was obtained with poly[3-(trimethylsilyl)-1-octyne] [Figure 1 (**6**)]. The left-hand onset ($V_s$) corresponds to the zero kinetic energy of the photoelectrons. The shift from $V_r = 0$ results from the work function difference between the sample and the collector. The right-hand onset ($V_0$) corresponds to the maximum kinetic energy ($E_k^{max}$) given by $E_k^{max} = e(V_0 - V_s)$. The ionization threshold energy ($I$) determined by the photoelectric emission from the highest occupied state of the polymer is given by $I = h\nu - E_k^{max}$, where $h\nu = 6.7$ or 8.41 eV in the present case. In the example of Figure 2, this gives a value of $I = 5.74$ eV. The lowest electronic excitation energy ($E_{ex}$) was deduced from the energy of the peak or shoulder in the UV−visible absorption spectrum of each polymer solution.[2,3,13−27] The observed values of $E_{ex}$ are listed in Table 1 together with the solvent used.

## III. Results and Discussion

Table 1 shows the ionization threshold energies of the polymers studied. To interpret these values, we consider a simple picture of the electronic structure of polyacetylene, a $\pi$-conjugated polymer, as shown in Figure 3a. The $\pi$ band derived from the interaction of the HOMO of the ethylenic unit forms the topmost part of the occupied states of polyacetylene. Similarly, the bottom part of the unoccupied states is formed by the $\pi^*$ band derived from the $\pi^*$ LUMO of the ethylenic part. In the first-order approximation for alternant aromatic hydrocarbons (e.g. by Hückel MO[28]), the occupied and unoccupied bands are symmetric with respect to the Fermi level, with the same bandwidth $W$.

Two effects are expected as a consequence of introducing substituents. First, the substitution causes steric hindrance

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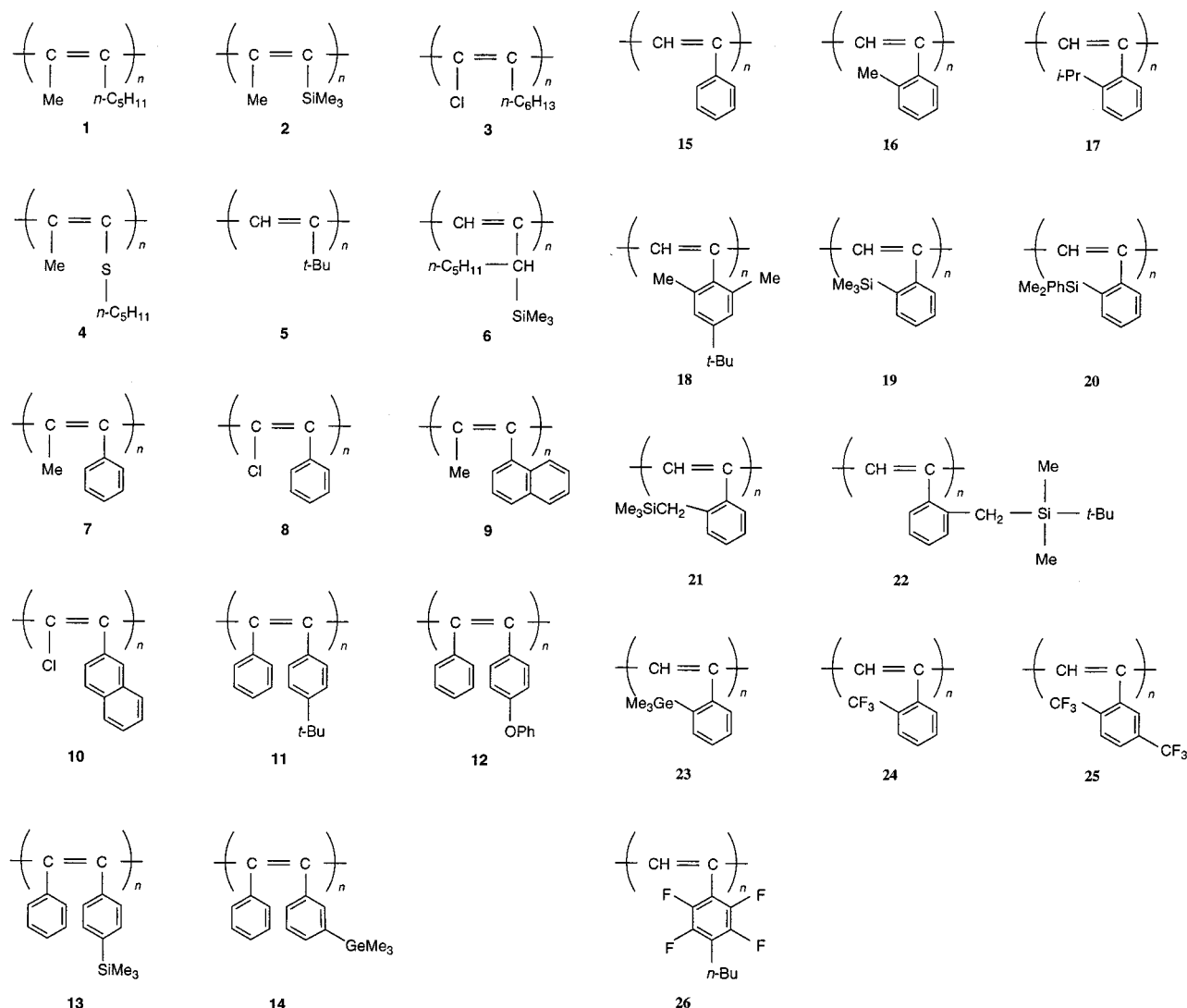† Nagoya University.
‡ Kyoto University.

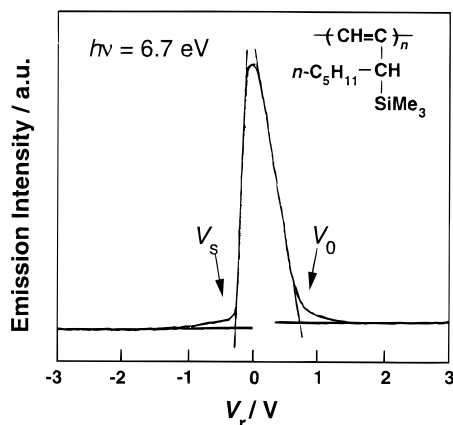**Figure 1.** Polymers examined in the present study.

**Figure 2.** UPS spectrum of poly[3-(trimethylsilyl)-1-octyne] (**6**).

among the substituents, leading to the breaking of the $\pi$-conjugation. As shown in Figure 3b, such a nonresonance effect (nR-effect) will reduce the bandwidths of the $\pi$ and $\pi^*$ bands by a similar amount. When we denote this reduction by $2\delta$, the ionization threshold energy $I$ is expected to increase by $\delta$ from the ionization threshold energy of unsubstituted polyacetylene $I^0$. We expect also an increase of the HOMO−LUMO bandgap ($E_g$) by $2\delta$ from the value for unsubstituted polyacetylene $E_g^0$. The bandgap can be estimated by the lowest energy of electronic excitation ($E_{ex}$) from the HOMO to the LUMO

measured by UV absorption spectra. Although we expect a small difference between $E_g$ and $E_{ex}$ due to the excitonic effect (Coulombic interaction between the electron in the LUMO and the hole in the HOMO), we can, as a first approximation, assume that this effect is roughly constant.

Second, the substituents are expected to cause an inductive effect (I-effect), as shown in Figure 3c. This leads to the simultaneous rise or lowering of the $\pi$ and $\pi^*$ levels by a similar amount $\delta'$. This results in a variation of $I$, while the excitation energy $E_{ex}$ will be virtually constant. Thus we can expect the following relationship for the changes of excitation energy $\Delta E_{ex}$ and that of the ionization threshold energy $\Delta I$ as a first approximation:

$$\Delta E_{ex} = 2\delta, \quad \Delta I = \delta \quad \text{(nR-effect)} \tag{1}$$

$$\Delta E_{ex} = 0; \quad \Delta I = \delta' \quad \text{(I-effect)} \tag{2}$$

and the resultant values of $E_{ex}$ and $I$ are expected to be

$$E_{ex} = E_{ex}^0 + 2\delta \tag{3}$$

$$I = I^0 + \delta + \delta' \tag{4}$$

This leads to the relationship between $E_{ex}$ and $I$

$$E_{ex} = 2I - 2\delta' + (E_{ex}^0 - 2I^0) \tag{5}$$

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**TABLE 1: Ionization Threshold Energies ($I$) and Electronic Excitation Energy ($E_{ex}$) of Substituted Polyacetylenes[a]**

| polymer | $I$/eV | $E_{ex}$/eV | solvent[b] | ref |
|---|---|---|---|---|
| *trans*-polyacetylene | 4.5 | 1.9 | | 10−12 |
| | 5.2 | | | |
| **1** | 5.6$_6$ | 4.43 | THF | 2 |
| **2** | 5.8$_7$ | 5.32 | THF | 3 |
| **3** | 6.9$_6$ | 4.59 | THF | 13 |
| **4** | 5.9$_3$ | 4.46 | CH | 13 |
| **5** | 6.0$_8$ | 4.38 | THF | 2 |
| **6** | 5.7$_4$ | 3.51 | CCl$_4$ | 15b |
| **7** | 5.9$_0$ | 4.35 | THF | 13 |
| **8** | 6.4$_9$ | 3.88 | THF | 13 |
| **9** | 5.7$_1$ | 4.28 | THF | 16 |
| **10** | 6.1$_4$ | 3.30 | THF | 17 |
| **11** | 5.2$_7$ | 2.95 | THF | 18 |
| **12** | 5.3$_3$ | 2.88 | THF | 19 |
| **13** | 5.4$_5$ | 2.88 | THF | 15a |
| **14** | 5.4$_4$ | 2.84 | THF | 20 |
| **15** | 5.4$_3$ | 3.16 | DCE | 21 |
| **16** | 5.1$_5$ | 2.66 | THF | 22 |
| **17** | 5.3$_2$ | 2.68 | CCl$_4$ | 23 |
| **18** | 5.0$_9$ | 2.40 | CCl$_4$ | 24 |
| **19** | 5.0$_9$ | 2.28 | THF | 24 |
| **20** | 4.8$_6$ | 2.34 | THF | 25 |
| **21** | 4.9$_7$ | 2.48 | CCl$_4$ | 26 |
| **22** | 5.1$_5$ | 2.34 | CCl$_4$ | 26 |
| **23** | 5.1$_5$ | 2.27 | THF | 27 |
| **24** | 5.3$_7$ | 2.77 | THF | 24 |
| **25** | 4.8$_5$ | 2.95 | DPDF | 22 |
| **26** | 5.6$_8$ | 2.90 | THF | 16 |

[a] All the $I$ values of the substituted polyacetylenes were measured in the present study. The values of $E_{ex}$ are taken from the reference. [b] The solvent used for the measurements of $E_{ex}$: THF, tetrahydrofuran; CH, cyclohexane; DCE, 1,2-dichloroethane; DPFB, *p*-bis(trifluoromethyl)benzene.
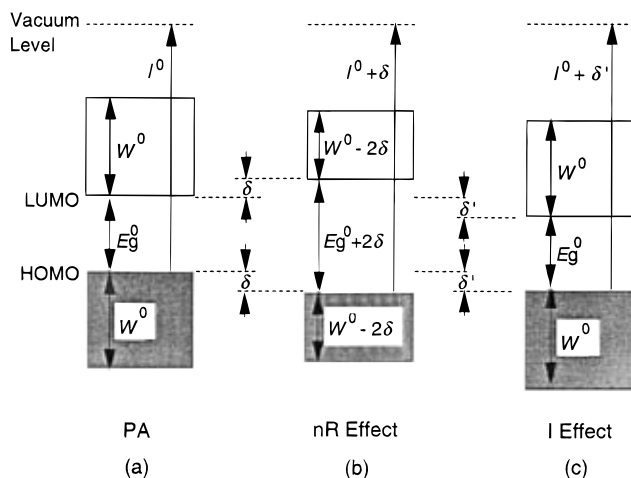
**Figure 3.** Schematic energy diagrams illustrating the effect of substituents for polyacetylene: (a) unsubstituted polyacetylene (PA), (b) "nonresonance" (nR) effect due to steric hindrance, and (c) inductive effect. $E_g$, $I$, and $W$ denote the bandgap, the ionization threshold energy, and the $\pi$ bandwidth, respectively, with the quantities with superscript 0 indicating the values for unsubstituted polyacetylene. $\delta$ and $\delta''$ are the change of $I$ induced by the substituent due to the nonresonance and inductive effect, respectively.

This implies that when the nR-effect is dominant, the slope of the $I$ vs $E_{ex}$ plot will be close to 2, while the I-effect will appear as a deviation from this linear relation. These points can be clearly seen from eqs 1 and 2.

To elucidate which of the two effects dominates, we plot the observed values of $I$ and $E_{ex}$ in Figure 4. The data for *trans*-polyacetylene (*t*-PA) is also shown. When we exclude the three polymers **3**, **8**, and **10** with Cl substituents at the main chain,
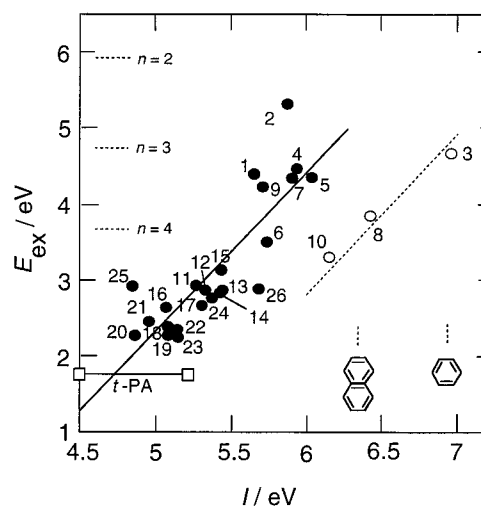
**Figure 4.** Relationship between the observed $I$ and $E_{ex}$ for substituted polyacetylenes (see Figure 1 for the numbers and polymer structures). The solid line shows the least-squares fit $E_{ex} = 2.11I − 8.22$ eV to filled circles corresponding to the polymers other than **3**, **8**, and **10**. The broken line shows the best fit $E_{ex} = 2.11I − 9.85$ eV with the same slope as the real line to open circles corresponding to the polymers **3**, **8**, and **10**, which have Cl atoms directly connected to the main chain. The open squares denote the reported results for *trans*-polyacetylene.[10−12] The horizontal lines at the top left indicate the electronic excitation energies of polyenes, with $n$ being the number of vinylene units.[38] The vertical lines at the bottom right denote the ionization threshold energies of polystyrene[11] and α- and β-poly(vinylnaphthalene)s.[36,37]

this plot provides a roughly linear relationship, which is expressed by

$$E_{ex} = 2.11I − 8.22 \text{ eV} \qquad (6)$$

The slope value in this equation is close to 2, implying that eq 1 essentially holds. The data for poly[(3,5-di-*tert*-butyl-4-hydroxyphenyl)acetylene] ($I = 5.5$ eV, $E_{ex} = 2.75$ eV), which we reported earlier, also fall near this line.[29] This finding clearly indicates that the effect of substitution appears predominantly as the consequence of the break of $\pi$-conjugation. The inductive effect may also affect the electronic structure, but only to a minor extent in these polymers. It is noted that the data of *t*-PA indicated by open circles in Figure 4 also lie on this line, although there is a rather large scattering between the two reported values of $I$.[10,12] This indicates that $\delta'$ is nearly zero, as seen from eq 5. The deviation of the observed values of $I$ from eq 6, which may be attributed to $\delta'$, is within 0.5 eV. It is also noted that a similar correlation between $I$ and $E_{ex}$ with a slope of 2 was found in substituted poly(*p*-phenylene vinylene)s.[30]

On the other hand, the polymers **3**, **8**, and **10**, which have Cl atoms directly bonded to the main chain, have larger $I$ values than do the polymers with similar $E_{ex}$. This indicates a significant contribution from the I-effect in these polymers by the strongly electron-withdrawing Cl atoms. Still the line has a slope value of nearly 2, assuming an equivalent slope value as that determined before (eq 6); a linear best fit yields the following:

$$E_{ex} = 2.11I − 9.85 \text{ eV} \qquad (7)$$

which again suggests that the nR-effect is operating in these polymers. The difference in the two lines in Figure 4 indicates a value of $\delta' = 0.8$ eV.

We can also confirm the validity of the above-described model by examining the constant second term in eq 7. Applying a simple Hückel model, which takes account of bond alternation

in polyenes, predicts $E_{ex}^0$ and $I^0$ in an isolated chain of polyacetylene to be

$$E_{ex}^0 = 2(k-1)\beta \qquad (8)$$

$$I^0 = -\alpha + (k-1)\beta \qquad (9)$$

where $\alpha$ is the Coulomb integral, $\beta$ is the resonance integral of the double bond, and the resonance integral of the single bond is taken to be $k\beta$. In the experiments for solid samples, the ionization energy is reduced by the electronic polarization of the surrounding molecules stabilizing the photoionized molecule.[6,31] When this polarization energy $P$ is taken into account, eq 8 is modified to

$$I^0 = -\alpha + (k-1)\beta - P \qquad (10)$$

Using typical values of $\alpha = -5.93$ eV,[32] $\beta = -2.88$ eV,[32] $k = 0.74$,[33] and $P = 1.7$ eV,[34] we obtain $E_{ex}^0 = 1.5$ eV and $I^0 = 5.0$ eV, which are in reasonable agreement with the observed values in Table 1 and Figure 4. From eqs 5, 8, and 10, we obtain

$$E_{ex} = 2I - 2\delta' + 2(\alpha + P) \qquad (11)$$

By assuming that $\delta' = 0$ and using the above-mentioned values, the sum of the second and the third terms is obtained to be 8.5 eV. Using this value and $I$ in the range of Figure 4, $E_{ex}$ determined from eq 11 agrees well with those of eq 6 within 0.3 eV. Such a good correspondence between theory and experiment verifies that the present analysis is essentially correct.

Based on the observed predominance of the nR-effect, we can estimate the reduction of the $\pi$ bandwidth $W$ to be about $2\delta$ (eq 3). According to UPS, the widths of $\pi$ and $\pi^*$ bands, $W^0$, in *trans*-polyacetylene is about 5 eV.[35] For the largest observed $\delta$ value of ca. 1 eV, the torsion of the main chain leads to a reduction of $W$ to about 3 eV, which is about 60% of the value for the unsubstituted polyacetylene.

Some conjugation between the main chain and the aromatic pendants may be expected. The observed results, however, indicate that introduction of the aromatic pendants does not lead to an effective conjugation, as seen from the increase of $E_{ex}$ from that of unsubstituted polyacetylene (1.9 and 2.0 eV for the *trans* and *cis* forms, respectively[35]). Except for samples **3** and **8**, the $I$ values for the present polymers are still significantly smaller than those of polystyrene (6.95 eV[11]) and $\alpha$- and $\beta$-poly(vinylnaphthalene)s (6.35 eV[36,37]), which are also shown in Figure 4. This finding indicates that the HOMO in these polymers is derived from the main chain of polyacetylenes and not from the $\pi$ orbitals of the phenyl or naphthyl pendants. Of the two remaining polymers, **3** has no aromatic pendant, while **8** has only a phenyl group in the repeating unit, which should have larger $I$ than the observed value of 6.51 eV. Therefore, the conclusion that the HOMO is derived from the main chain applies also to these polymers.

The $E_{ex}$ values observed give a measure of the degree of breaking of the conjugation. In Figure 4 the excitation energies of polyenes with $n$ double bonds in the trans form are shown for $n = 2$ (butadiene), 3 (hexatriene), and 4 (octatetraene).[38] The maximum $E_{ex}$ observed in the present study corresponds to $n = 3$, indicating that the degree of effective conjugation in extensively twisted polymers is similar to that in hexatriene.

When both the ionization energies and absorption spectra are considered, it is concluded that significant variations of the energy parameters in substituted polyacetylenes come from various degrees of the breaking of conjugation, probably caused by the steric hindrance. An inductive effect was also observed on substitution by strongly electron-withdrawing Cl atoms. The pendent groups act as the protecting groups against the degradation by air, but at the same time break the conjugation to some extent and also block the dopant from affecting the electronic structure of the conjugated main chain. More detailed discussion of the steric hindrance is difficult at present, owing to the lack of direct structural information for these polymers. However, the picture depicted about the role of pendent groups gives information useful to the development of electronically functional substituted polyacetylenes.

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