

SHORT COMMUNICATIONS

UPS Spectra of the Polyacetylene Derivatives Carrying Stable Radical Substituents

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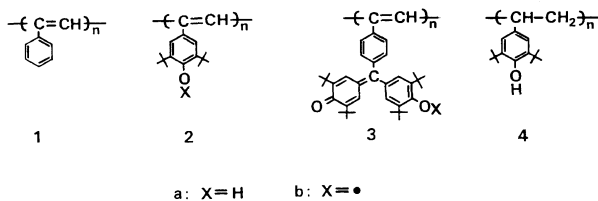
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Substituted polyacetylenes have recently attracted much attention due to their electrical conduction<sup>1-3</sup> and photo conduction<sup>4</sup> based on their  $\pi$ -conjugation along the main chain. Recently there arises the possibility of unique magnetic interaction for polyacetylenes carrying stable radical substituents<sup>5,6</sup> and several model compounds have been reported.<sup>7-9</sup> The electronic structure of main chain is quite important for discussing the magnetism of these polyradical macromolecules such as **2b** and **3b** (Scheme 1) because magnetic interaction is expected to occur through the  $\pi$ -conjugated main chain. While the existence of  $\pi$ -conjugation along the main chain with alternating single and double bonds in some substituted polyacetylenes is demonstrated by UV/VIS spectroscopy,<sup>10-12</sup> detailed investigation using other spectroscopy has not been

performed yet. Ultraviolet Photo Electron Spectroscopy (UPS) is suitable for a detailed study of the uppermost part of the valence states of organic polymers, which is most important in discussing the electronic properties of them.

In this communication, we report on the correlation between UV/VIS absorption and ionization threshold ( $I^{\text{th}}$ ) from UPS and on the effect of substituents of phenyl ring. While the UPS spectroscopy was applied to many organic polymers<sup>14</sup> including unsubstituted polyacetylene, there is no report on substituted polyacetylenes as yet.

Poly[(3,5-di-*tert*-butyl-4-hydroxyphenyl)acetylene] (**2a**) and poly(*p*-ethynylphenylhydrogalvinoxyl) (**3a**) are prepared as described in ref 7 and 8, respectively. These polymers were carefully oxidized with freshly prepared



Scheme 1.

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PbO<sub>2</sub> or alkaline K<sub>3</sub>Fe(CN)<sub>6</sub> in benzene under oxygen-free atmosphere to give corresponding polyradicals (**2b**, **3b**). Spin concentration of polyradical was determined by the comparison of the ESR signal area of the benzene solution of 2,2,6,6-tetramethyl-1-piperidinoxyl, with known spin concentration (98%, Aldrich). Poly(phenylacetylene) (PPA) (**1**) was prepared according to lit. 13. Poly(3,5-di-*tert*-butyl-4-hydroxystyrene) (**4**) was gifted from Maruzen Sekiyu Co. These polymers were spin-coated on a polished copper electrode. UPS spectra were measured on an apparatus similar to that in lit. 14. It consists of a Xe I (8.42 eV) light source and a retarding field type analyzer with a resolution of *ca.* 0.2 eV.

UPS spectra of **2a** and **4** were shown in Figure 1. The values of  $I^{\text{th}}$  of these polymers are summarized in Table I. These peaks are unimodal and fine structure are not observed. The  $I^{\text{th}}$  of **2a** is between that reported for *trans*-polyacetylene<sup>15</sup> and that of **1**. This observation agrees with the trend in the visible spectra: the absorption maximum of **2a** is in the visible region ( $\lambda_{\text{max}} = 450 \text{ nm}$ ,  $\epsilon = 38001/\text{monomer mol cm}^{-1}$ ), while that of **1** is in the ultraviolet region (Figure 2) indicating that the degree of conjugation around the main chain in **2a** is larger than that of **1**. The  $I^{\text{th}}$  of **4** (6.3 eV) is well reproduced if  $I^{\text{th}}$  of polystyrene (6.95 eV, solid phase)<sup>16</sup> is corrected by use of the difference in  $I^{\text{th}}$  between benzene (9.24 eV gas phase)<sup>17</sup> and phenol (8.7 eV, gas phase).<sup>17</sup> The smaller  $I^{\text{th}}$  of **2a** than that of **4** confirms that the highest occupied orbital in **2a** contains

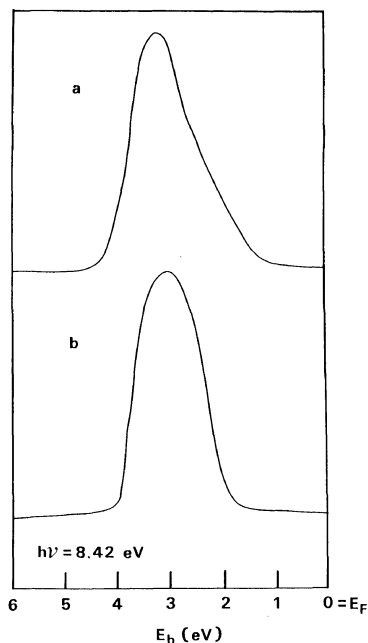


Figure 1. UPS spectra of **2a** (a) and **4** (b).

Table I. Ionization threshold energies ( $I^{\text{th}}$ ) of 1–4

Polymer	Cat./Solv.	$\bar{M}_n^a \times 10^{-4}$	$I^{\text{th}}$ eV
<b>1</b>	WCl <sub>6</sub> /Bz	1.4	5.7
<b>2a</b>	WCl <sub>6</sub> /CCl <sub>4</sub>	1.8	5.5
<b>2a</b>	MoCl <sub>5</sub> /Bz	1.4	5.5
<b>3a</b>	Rh <sup>b</sup> /THF	2.0	5.9
<b>4</b>	—	1.5	6.3

<sup>a</sup> Determined by GPC (PSt standard).

<sup>b</sup> [RhCl(C<sub>8</sub>H<sub>12</sub>)<sub>2</sub>].

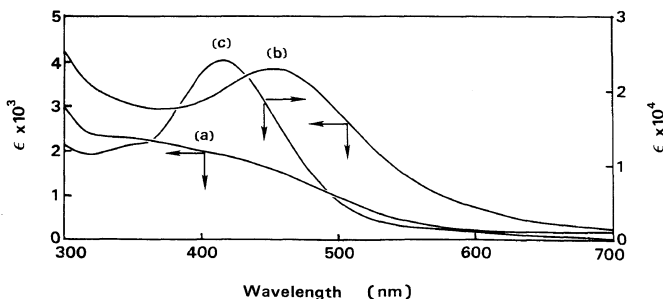


Figure 2. UV/VIS spectra of **1** (a), **2a** (b), and **3a** (c) in CH<sub>2</sub>Cl<sub>2</sub>.

the contribution from the main chain, indicating an efficient development of  $\pi$ -conjugation along the polyacetylene main chain.

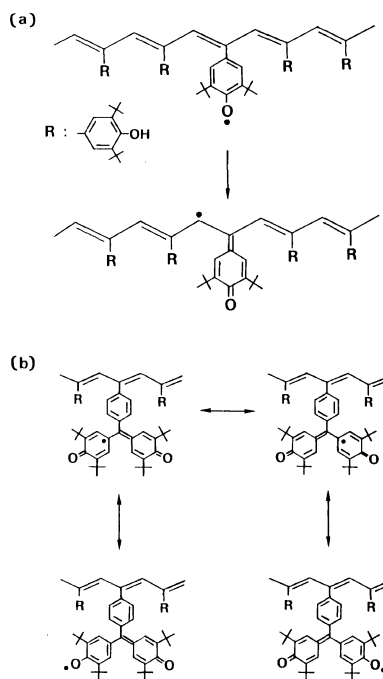
**3a** has  $\lambda_{\max}$  at 420 nm due to the presence of quinoid chromophore in the side chain. This absorption continues to 550 nm which is about 30 nm longer than that of corresponding monomer, indicating the presence of some  $\pi$ -conjugation along the main chain.  $I^{\text{th}}$  of **3a** is higher than that of **1**, indicating  $\pi$ -conjugation does not develop in **3a** compared with **1**.

Thus **2a** and **3a** show increase and decrease of the degree of  $\pi$ -delocalization compared to **1**, respectively. The increase in **2a** may come from factors such as steric hindrance among the substituents to prevent the free rotation of the phenyl ring in a way favoring planar main chain structure and/or the chain-substituent interaction, and (2) the lowering of the ionization energy of the substituent from **1**, which should increase the degree of mixing with the main chain by reducing the energy difference between the chain and the substituent. The decrease in **3a** may be explained by the steric hindrance to prevent the effective chain-substituent mixing and/or intrachain conjugation. Further studies are necessary for clarifying these points.

The  $I^{\text{th}}$  of polyradical derivatives **2b** and **3b** are listed in Table II.  $I^{\text{th}}$  of **2b** is greatly increased from that of **2a** (5.5 eV) to 6.4 eV, indicating that conjugation length along the main chain is decreased with oxidation. It can be explained by the migration of unpaired spin<sup>7</sup>: solution ESR spectra of **2b** indicated that the formed unpaired spin migrates to the main chain, then the phenoxy structure changes to quinone methide structure which deconjugates the main chain (Scheme 2(a)). On the other hand,  $I^{\text{th}}$  of **3b**s are almost constant irrespective of spin concentration and not significantly different from that of **3a**. Because the formed unpaired spin is delocalized within galvinoxyl skeleton in **3b** (Scheme 2(b)) evidenced by the

**Table II.** Ionization threshold energies ( $I^{\text{th}}$ ) of **2b** and **3b**

Polymer	Spin concn	$I^{\text{th}}$
	mol%	eV
<b>2b</b>	8	6.4
<b>3b</b>	23	6.1
<b>3b</b>	39	6.1
<b>3b</b>	62	6.1



**Scheme 2.**

solution ESR spectra in ref 8, the electronic state of main chain is not affected with the formation of unpaired spin. From these findings, spin localized profile in the side chain seems to be superior to spin-delocalized one in **3b**.

In summary, in this communication we have shown the existence of significant  $\pi$ -conjugation along the main chain in poly(phenylacetylene)s by UPS and also examined their substituent effects.

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## REFERENCES

1. G. Polzonetti, V. Faruffini, A. Furlani, and M. V. Russo, *Synth. Met.*, **25**, 375 (1988).
2. P. Cukor, J. I. Krugler, and M. F. Rubner, *Makromol. Chem.*, **182**, 165 (1981).
3. G. M. Holob and P. Ehrlich, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 627 (1977).
4. E. T. Kang, P. Ehrlich, A. P. Bhatt, and W. A. Anderson, *Macromolecules*, **17**, 1020 (1984).
5. A. A. Ovchinnikov, *Theoret. Chim. Acta*, **47**, 297 (1978).
6. N. Tyutyulkov, *Chem. Phys.*, **112**, 293 (1987).
7. H. Nishide, N. Yoshioka, K. Inagaki, and E. Tsuchida, *Macromolecules*, **21**, 3119 (1988).
8. H. Nishide, N. Yoshioka, T. Kaneko, and E. Tsuchida, *Macromolecules*, **23**, 4487 (1990).
9. A. Fujii, T. Ishida, N. Koga, and H. Iwamura, *Macromolecules*, **24**, 1077 (1991).
10. T. Masuda, T. Hamano, K. Tsuchihara, and T. Higashimura, *Macromolecules*, **23**, 1374 (1990).
11. J. Kunzler and V. Percec, *J. Polym. Sci., Polym. Chem. Ed.*, **28**, 1221 (1990).
12. Y. Abe, T. Masuda, and T. Higashimura, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 4267 (1989).
13. T. Masuda, T. Hamano, T. Higashimura, T. Ueda, and H. Muramatsu, *Macromolecules*, **21**, 281 (1988).
14. K. Seki, "Photoelectron Spectroscopy of Polymers" in "Optical Techniques to Characterize Polymer Systems," H. Baessler, Ed., Elsevier Science Publishers, Amsterdam, 1989, p 115.
15. J. Tanaka, M. Tanaka, H. Fujimoto, M. Shimizu, N. Sato, and H. Inokuchi, *J. de Phys.*, **C3**, 279 (1983).
16. N. Fujihira, T. Hirooka, and H. Inokuchi, *Chem. Phys. Lett.*, **19**, 584 (1987).
17. "Handbook of He I Photoelectron Spectra of Fundamental Organic Molecules," K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, Ed., Japan Scientific Societies Press, Tokyo, 1981.