Correlation between ESCA and NMR Chemical Shifts of Carbons in Linear Polymers

Shoji SUZUKI, Yoshio INOUE, Isao ANDO, Riichirô CHÛJÔ

*Department of Polymer Chemistry, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152, Japan.*

Kazuyoshi SETO, and Kiyoshi HOSHINO

*Kokusai Electric Co., Ltd., 1-1 Shimmeidai 2-chome, Hamura-cho,
Tokyo 190-11, Japan.*

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ABSTRACT: ESCA spectra in CK region were measured for several kinds of linear polymers; corrections for the influence of charging were made. The chemical shifts (ΔE_b) in the ESCA spectra observed were compared with the chemical shifts (δ_c) in ^{13}C NMR and electron densities (ED). There are generally good linearities in both comparisons with only a few exceptions. Two kinds of linear relations can be deduced in the ESCA data and one in the ED . One ESCA relation is deduced from all the data observed and the other from the data of the aliphatic groups alone. The linear relations are:

$$\Delta E_b = -0.029\delta_c + 4.35 \quad (\text{whole})$$

$$\Delta E_b = -0.045\delta_c + 6.85 \quad (\text{aliphatic})$$

$$\Delta E_b = -9.43ED + 37.38$$

We can safely say that there are linear relations between CK ESCA and ^{13}C NMR chemical shifts, and between ESCA chemical shifts and electron densities. These linear relations serve for the assignment of peaks in the course of ESCA studies.

KEY WORDS Electron Spectra / ESCA / NMR / Electron Density /
Aliphatic Group / Poly(vinyl alcohol) / Polystyrene / Contamina-
tion / Charging / Evaporation Method /

ESCA (Electron Spectroscopy for Chemical Analysis) is one of the analytical instruments which has rapidly advanced in recent years. It is a technique for determining the binding energies of inner shell electrons so that the chemical structure of a molecule can be determined from its chemical shift. ESCA seems to be a very useful technique for obtaining information on polymer configuration and conformation when it is applied to polymer systems. In order to analyse ESCA spectra precisely the assignment of each peak in the spectra to a corresponding configuration or conformation must be carried out. Such assignments have not been completed as yet. One of the purposes of this report is to obtain some information about assignments of ESCA chemical shifts by using

NMR (Nuclear Magnetic Resonance) chemical shifts. Several investigations have been made to study the correlation between ESCA and NMR chemical shifts in low-molecular-weight compounds.¹⁻⁴ We will also examine the correlation between ESCA chemical shifts and electron densities, because it can be expected that the binding energy will decrease when the electron density around the atom increases. There have been only a few ESCA studies of polymers; polyethylene and others,⁵ the helix-coil transition of poly(γ -benzyl L-glutamate),⁶ the crystallinity of fluorine-containing polymers,⁷ the surface oxidation of wool⁸, fluorine-containing polymers,^{9,10} and nitroso rubbers.¹¹

The fact that there have been only a few studies about the ESCA spectroscopy of polymers

implies that the comparison of ESCA chemical shifts with NMR chemical shifts and electron densities can assist in the assignment of peaks observed in the course of ESCA research.

EXPERIMENTAL

Apparatus

ESCA spectra were measured with a Kokusai/AEI ES-100 electron spectrometer.

Sample

The sample polymers were the ones used in the ^{13}C NMR study, for convenience in comparison with NMR chemical shifts. Detailed descriptions are given elsewhere¹²⁻¹⁸ except for poly(ethylene glycol). Poly(ethylene glycol), lot 805130, was purchased from Nippon Oil & Fats Co., Ltd. Samples used are as follows:

Polyacrylonitrile (PAN), poly(vinyl alcohol) (PVA), poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC), polystyrene (PSt), poly(ethylene glycol) (PEG), polyethylene (PE), poly(vinyl acetate) (PVAc) and polypropylene (PP). All samples were used in solid state, whose forms are as follows:

powder.....PAN, PVC, PSt, PEG, PP
bulkPVA, PMMA, PVAc
grain.....PE

Procedure

The aluminum $\text{K-}\alpha_{1,2}$ (1486.6 eV) and the magnesium $\text{K-}\alpha_{1,2}$ (1253.6 eV) radiation were used as the X-ray excitation sources. The X-ray power supply was run at 12 kV and 25 mA. Spectra were measured at room temperature.

RESULTS AND DISCUSSION

Typical CK ESCA spectra are reproduced in Figures 1—3. The CK ESCA chemical shifts obtained are summarized in Table I.

Interpretation of PSt Spectrum

Figure 2 is the PSt spectrum, which is different from those of the other polymers; only one peak appears. This peak can be assigned to phenyl carbon because of its relatively large intensity. On the other hand, peaks of methine and methylene carbon should appear in this region (see Table I), so all peaks seem to have coalesced into this large peak. The peak intensity is proportional to the corresponding number of atoms. For example, in the case of

Figure 1. High-resolution ESCA spectrum of poly(vinyl alcohol) sample in CK region by $\text{Mg-K}\alpha$ radiation. Counting rate of the spectrum is about 10^8 cps at the maximum point.

Figure 2. High-resolution ESCA spectrum of polystyrene sample in CK region by Al-K α radiation. Counting rate of the spectrum is about 5×10^8 cps at the maximum point.

Figure 3. High-resolution ESCA spectrum of poly(vinyl acetate) sample in CK region by Al-K α radiation. Counting rate of the spectrum is about 4×10^8 cps at the maximum point.

PVAc, the relation of 1:1:1:1 is established between four peaks, *i.e.*, methyl, methylene, methine, and carbonyl carbons, as shown in Figure 3. Another weak plateau appears in a position 7 eV higher in binding energy than the main peak, as seen in Figure 2. A similar phenomenon is seen in the spectrum of poly(α -methylstyrene), but the origin is as yet unknown.

Influence of Contamination and Charging

One of the disadvantages of ESCA spectra in the carbon and oxygen region is the possible coalescence of the spectra due to contamination of dust and oil in the instrument. In this experiment we cannot detect any such contamination influence. So even if there does exist some influence of contamination, its effect is not so

Table I. CK ESCA chemical shifts in linear polymers^a

No.	Polymer	Chemical species	CK ESCA chemical shift, eV
1	Polyacrylonitrile	Methylene	-0.6
2		Methine	0.3
3		Cyano	1.0
4	Poly(vinyl alcohol)	Methylene	-0.5
5		Methine	1.0
6	Poly(methyl methacrylate)	Carbonyl	3.6
7		Others	-0.4
8	Poly(vinyl chloride)	Methylene	-0.6
9		Methine	0.8
10	Polystyrene	Phenyl	-0.7
11	Poly(ethylene glycol)	Methylene	1.0
12	Polyethylene	Methylene	0.0
13	Poly(vinyl acetate)	Methyl	-0.8
14		Methylene	0.0
15		Methine	1.2
16		Carbonyl	3.7
17	Polypropylene	All	-0.4

^a The methylene carbon peak in polyethylene is adopted as the reference for chemical shifts. "Others" of PMMA and "All" of PP in the column of chemical species mean the average value of methylene, methyl, α -sketal, and methoxy carbons in the former, and methylene, methyl, and methine carbons in the latter.

large as to change the line shape of the spectra. Another disadvantage occurs when the samples

are insulators like polymers, namely, a shift to the lower kinetic energy side due to charging. In order to correct this effect, gold was evaporated in vacuum on the sample surface.¹⁹ We can safely say that this technique is useful for correcting the influence of charging. The values of binding energies in Table I are ones corrected by this technique.

Correlation between ESCA and NMR Chemical Shifts

Recently Swartz and Hercules¹ investigated the correlation between ESCA and NMR chemical shifts of quaternary phosphonium compounds, and they indicated that a linear relation holds in general, with a few exceptions. Basch²⁰ and Zevoka²¹ theoretically derived a similar relation. The information obtained from ESCA

and from NMR may be considered analogous in some sense, because ESCA measures the electrostatic shielding of a photoelectron, while NMR measures the magnetic shielding of a nucleus from an external field by electrons.

Figure 4 is a plot of CK ESCA chemical shifts against ¹³C NMR chemical shifts. The latter values were adopted from previous reports.¹²⁻¹⁸ The straight lines (1) and (2) are obtained using a least square fit to all data in Table I except for point 10, and points 3, 6, 10, and 16, respectively. If we can adopt the line (1) as a linear relation between ESCA and NMR chemical shifts, the datum from aromatic carbon (No. 10) does not fall on this line, while if the line (2) is adopted, the data from carbons with double- or triple-bonds (3, 6, 10, and 16)

Figure 4. Correlation between CK ESCA chemical shifts and ¹³C NMR chemical shifts in linear polymers. The carbon peak of CS₂ is adopted as the reference for NMR chemical shifts. Numbers in this figure are identical with those in Table I.

do not fall on this line. This may be explained as follows. Owing to the delocalized π -electrons, the binding energies of carbons with unsaturated bonds become smaller than those expected for an aliphatic group. Which line is more appropriate is a question for further study. We can now safely say that a more or less linear relationship holds between CK ESCA chemical shifts and ^{13}C NMR chemical shifts of polymers. From Figure 4 we have the following equations between ESCA chemical shifts ΔE_b and NMR chemical shifts δ_c in the polymers examined:

$$\Delta E_b = -0.029\delta_c + 4.35 \quad (\text{from line (1)})$$

$$\Delta E_b = -0.045\delta_c + 6.85 \quad (\text{from line (2)})$$

Correlation between ESCA Chemical Shifts and Electron Densities

ESCA chemical shifts are usually explained by the electronegativities of the substituted groups.^{22,23} Generally in simple molecules this

explanation succeeds fairly well, but in more complex molecules agreement between experimental data and calculated points is not so good. For polymers no study of the correlation between ESCA chemical shifts and electron densities has been published. Figure 5 is a plot of CK ESCA chemical shifts against electron densities of model compounds (2,4-disubstituted pentane) calculated by CNDO/2 method, except for PVC (extended Hückel method).²⁴ A straight line can be drawn using a least square method to all data in Figure 5. As a whole a linear relation holds. These calculated electron densities are only for $2s$ and $2p$ orbital electrons in carbon, while ESCA chemical shifts are for CK electrons. The slope of the straight line is in the sense which one would theoretically predict, since the larger electron density yields the lower binding energy, *i.e.*, the smaller ESCA chemical shift. From this figure, we have the following equation between ESCA chemical

Figure 5. Correlation between CK ESCA chemical shifts and electron densities of the model compound. Electron densities are calculated by CNDO/2 method, except for PVC (extended Hückel method). Numbers in this figure are identical with those in Table I.

Figure 6. Correlation between ^{13}C NMR chemical shifts and electron densities of the model compound. In this figure No. 17a, 17b, and 17c mean methyl, methylene, and methine, carbon in polypropylene, and No. 17 is the average of these three values. Numbers in this figure are identical with those in Table I.

shifts ΔE_b and electron densities ED :

$$\Delta E_b = -9.43ED + 37.38$$

Correlation between NMR Chemical Shifts and Electron Densities

Figure 6 is a plot of ^{13}C NMR chemical shifts against electron densities. The straight line was drawn using a least square method to all data in Figure 6 except for points 3 and 8. As a whole linear correlation is not seen; none the less, the larger electron densities yield the higher NMR chemical shifts, because the magnetic shielding of the atom increases. The equation of this line is

$$\delta_c = 323ED + 1120$$

Point No. 3 is particularly far away from the straight line and it thus contrasts with the agreement in Figure 5. So another factor may exist in NMR chemical shifts.

CONCLUSIONS

1. To correct the influence of charging of insulator-like polymers it is useful to evaporate metals like gold over the sample surface.
2. Two possible equations are found between ESCA chemical shifts ΔE_b and NMR chemical shifts δ_c , as follows:

$$\Delta E_b = -0.029\delta_c + 4.35 \quad (\text{from line (1)})$$

$$\Delta E_b = -0.045\delta_c + 6.85 \quad (\text{from line (2)})$$

It must be determined later which line is more appropriate.

3. One equation is found between ESCA chemical shifts ΔE_b and electron densities ED , as follows:

$$\Delta E_b = -9.43ED + 37.38$$

This relation holds good even for the carbons with unsaturated bonding studied in this report. The question whether all polymers obey the above relationship must await further experiments.

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