Ultraviolet Photoelectron Spectroscopy of Some Fundamental Vinyl Polymers and the Evolution of Their Electronic Structures

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UV photoelectron spectra were measured for polypropylene (PP), poly(vinyl fluoride) (PVF), 1,2-polybutadiene (1,2-PBD), poly(vinyl chloride) (PVC), and poly(vinyl alcohol) (PVA). Their threshold ionization energies were found to be 8.5, 9.2, 7.5, 8.8, and 8.0 eV (1 eV≅0.1602 aJ), respectively. The evolution of their electronic structures (from those of small related molecules) were analyzed, mainly, by using the photoelectron spectra of these small compounds (including the new data of 1,2-propanediol). The data of previously measured polyethylene (PE) and polystyrene (PS) were analyzed together. With the results, the polymers were classified into three groups according to the increasing order of localization of the positive hole in the cationic state: (1) PE, PP, and PVF, (2) 1,2-PBD, PVC, and PVA, and (3) PS as a representative of aromatic-pendant polymers.

Ultraviolet photoelectron spectroscopy (UPS) has been developed as a powerful tool in studying the electronic structure of organic solids.[1-4] In particular, an important quantity obtainable by UPS is the threshold ionization potential of a solid, which gives the location of the top of a valence band. Together with the energy of the bottom of a conduction band, it gives a basic picture of the electronic structure of a solid. However, so far studies of organic polymers by UPS have been concentrated on polymers with aromatic groups,[5,6] polyethylene (PE) and its model compounds,[7] and some conducting polymers.[8] There seems to be no report on vinyl polymers with pendants other than aromatic rings, except for a relevant report by Vilesov *et al.*[9] on the photon-energy dependence of the photoemission quantum yield. Pireaux *et al.*[10] reported an X-ray photoelectron spectroscopy (XPS) study of vinyl polymers, but the low intensity and the broadness of the spectral features prevented a detailed study of the valence bands.

In this work, we report a UPS study regarding a series of vinyl polymers $\{CH_2CHX\}_n$ with non-aromatic pendant X, *i.e.*, polypropylene (PP, X:CH_3), poly(vinyl fluoride) (PVF, X:F), 1,2-polybutadiene (1,2-PBD, X:$CH{=}CH_2$), poly(vinyl chloride) (PVC, X:Cl), and poly(vinyl alcohol) (PVA, X:OH).

Our aims are (1) to obtain reliable experimental data regarding threshold ionization energy, and (2) to interpret the observed threshold energies (and other spectral features) in terms of intramolecular and intermolecular factors. The results of previously measured polyethylene (PE, X:H)[7a] and polystyrene (PS, X:C_6H_5)[5a] were also analyzed.

For aim (2), the electronic structure of an isolated single polymer chain is used as the base of interpretation. The intermolecular contribution can be deduced by comparing it with the observed solid state results. Unfortunately, however, the gaseous state of a polymer is not realizable, and theoretical calculations are not quantitatively reliable, either. In order to overcome this difficulty, we estimated the electronic structure of an isolated chain from the gas-phase photoelectron spectra of related small molecules by analyzing the pendant-chain and also pendant-pendant interaction. Since no information in the literature was available for 1,3-propanediol, which is related to PVA, we measured its gas-phase photoelectron spectrum. Theoretical band calculations for an isolated polymer chain[10-13] and solid XPS results[10] also helped in the interpretation for some polymers.

This method of analysis shows how the electronic structures of polymer solids evolve from those of small units. The results indicate various patterns of evolution, depending on the polymers. In particular, the degree of delocalization of the positive hole in the cationic state ranges from almost complete localization in a pendant to extensive delocalization over the principal chain. Although rather rough approximations are involved in the present treatment, we believe it gives a general viewpoint for analyzing the electronic structures of polymers.

Experimental

Standard samples of PP (isotactic), PVF, PVC, and PVA were available from Scientific Polymer Products Inc. (catalog Nos. 130, 022c, 038c, and 002, respectively). Low-crystallinity 1,2-PBD was provided by Japan Synthetic Rubber Company. PP was twice reprecipitated from a decalin solution with cyclohexane as a poor solvent; PVF twice from *N,N*-dimethyl formamide (DMF) with methanol; PVC three times from tetrahydrofuran (THF) with methanol; and 1,2-PBD once from a benzene solution with methanol. PVA was used without further purification.

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The UPS spectrometer consists of a light source and a retarding-potential-type electron energy analyzer, which was reported previously.[14] Two kinds of light sources were used. One was hydrogen discharge lamp attached to a 0.5 m Seya-Namioka-type monochromator and the other was a rare-gas resonance lamp capable of He I (21.2 eV), Ne I (16.8 eV), and Ar I (11.7 eV) emissions. The same ionization energies were obtained by both two light sources.

Since these polymers are insulators, we had to use thin film samples to avoid charging. The films were prepared by putting a few drops of a hot solution (≈0.2 wt%) of a polymer on a Cu-disk (12 mm diameter) substrate, followed by the rotation of the substrate. The rotation spreaded the solution, and the solvent vaporized, leaving a thin film.[15] The temperatures of the solution and the substrate were kept at 60—70 °C except for the case of 1,2-PBD, where the film was prepared at room temperature. The solvents used for PP, PVF, 1,2-PBD, PVC, and PVA were decalin, DMF, benzene, DMF, and redistilled water, respectively.

In this sample preparation procedure, we paid close attention to the suppression of the emission from the substrate, because the threshold energy of the substrate was inferred to be smaller than those of polymers. This requires both a good uniformity of the film and a sufficient average thickness. We found that the uniformity significantly depends on the adhesive property of the solution to the substrate. For example, PVC films of poor (net-like) quality were obtained from THF solution even if a large amount of solution was used, while a uniform film was obtained by using DMF and heating the substrate and the solution. After choosing appropriate solvents, we increased the amount of deposited polymer sample until there was no further change in the spectrum. The concentration and procedures described above gave satisfactory films for getting an intrinsic spectra of the polymers without charging, although we had to use very weak light for some specimens in order to avoid charging. The nominal average thickness of a film was ≈2 μm, but the polymers tended to accumulate at the periphery of a substrate surface when the solvent vaporized away. Therefore, the real average thichness on a substrate surface should be smaller. The absence of charging was verified by the sharpness of the cut off at the low-kinetic-energy side of the spectra.

The He I gas-phase photoelectron spectrum of 1,3-propanediol was measured on the photoelectron spectrometer which was reported previously.[16]

Results and Discussion

Threshold Ionization Energies. In Figs. 1—5, the photoelectron spectra of the polymers are shown. The abscissa represents the solid ionization energy I_s, which is related to the kinetic energy of a photoelectron by $I_s=h\nu-E_k$, where $h\nu$ is the photon energy. The values of the threshold ionization energy are given by $I_s^{th}=h\nu-E_k^{max}$, where E_k^{max} is the maximum kinetic energy of photoelectrons. They are listed in Table 1. These values are the averages of at least six times measurements for each compound. The standard deviation was less than 0.2 eV. Table 1 also lists our previous data for high-density PE[7a] and PS,[5a] the

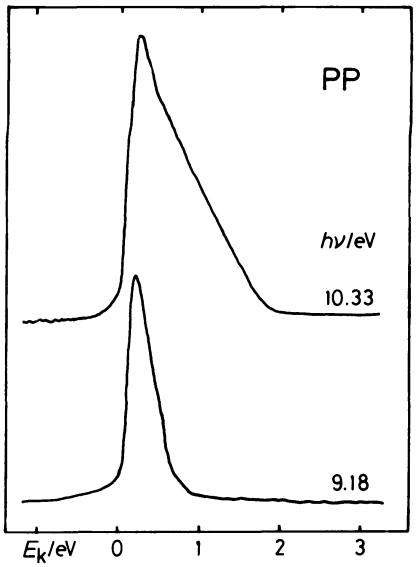

Fig. 1. Photoelectron spectra of polypropylene. The photon energy of the exciting light is shown at the side of each curve.

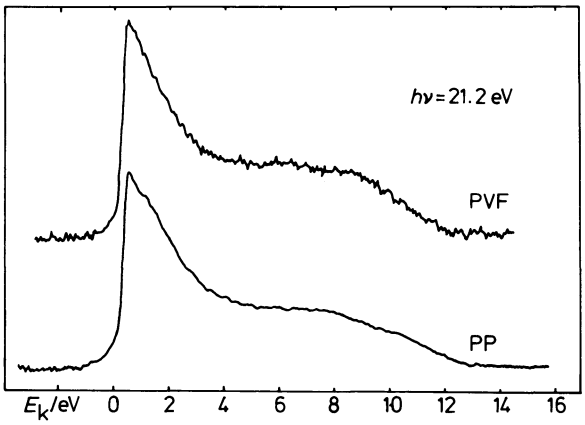

Fig. 2. Photoelectron spectra of poly(vinyl fluoride) and polypropylene by He I (21.2 eV) light source.

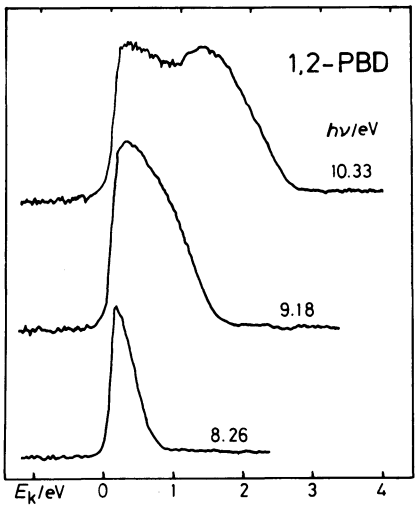

Fig. 3. Photoelectron spectra of 1,2-polybutadiene. The photon energy of the exciting light is shown at the side of each curve.

assignment of the character of the HOMO (discussed below), the threshold (adiabatic) ionization energies of the corresponding "unit" compounds CH_3CH_2X in the gas phase I_g^a(unit),[16-18] and the difference $\Delta I = I_g^a(\text{unit}) - I_s^{th}$. (Pireaux *et al.*[10] used $CH_2=CHX$ for the unit compound, but this is inadequate since the character of the highest occupied orbital can change from the π orbital in $CH_2=CHX$ to σ or lone pair orbitals in the polymer, as shown below).

Vilesov *et al.*[9] reported the I_s^{th} values of PVA, PVC, poly(*N*-vinylcarbazole) (PVCz), and PS to be 6.0, 6.0, 5.8, and 7.0 eV, respectively. The values for PVA and PVC are much lower than the present results, while those for PVCz and PS are in good agreement with our results (5.85 eV[5d] and 6.95 eV[5a] obtained with the present instrument). Since the preparation of uniform films was more difficult for PVA and PVC than for polymers with aromatic pendants, we may conclude that the data by Vilesov *et al.* are questionable for PVA and PVC.

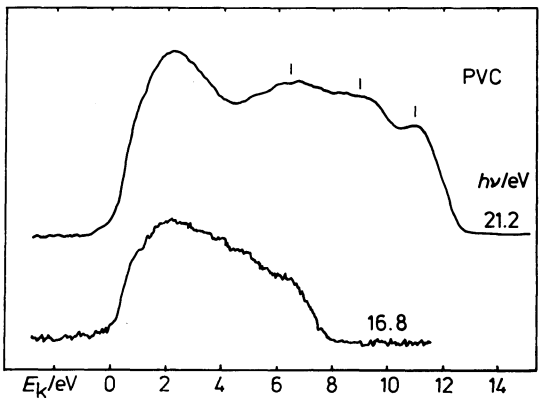

Fig. 4. Photoelectron spectra of poly(vinyl chloride) by He I (21.2 eV) and Ne I (16.8 eV) light sources.

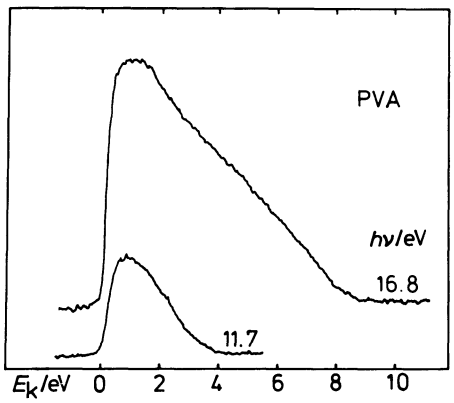

Fig. 5. Photoelectron spectra of poly(vinyl alcohol) by Ne I (16.8 eV) and Ar I (11.7 eV) light sources.

Pireaux *et al.* reported XPS data on the location of the top of the valence band for some of these polymers,[10] but threshold energies derived from their data with estimated work functions ($E_1+\phi$ in Table 6 of Ref. 10) are 0.5–2 eV larger than the present directly-measured values.

Method of Analysis. It is known that for molecular solids, a solid photoelectron spectrum resembles the gas-phase spectrum of the compound if a shift is made in the ionization-energy scale.[19] The similarity indicates the preservation of the electronic structure of a molecule in a solid, and that the photoemission from a molecular solid can be regarded as the ionization of a molecule in the solid. The shift can be attributed to the stabilization of the molecular cation by the polarization of the surrounding molecules; hence, it is called the polarization energy P.[1,4c] According to an analysis of the contribution of molecules in the bulk and at the surface, we already noted that the bulk polarization energy can be evaluated as the difference of the threshold energies of the gas and solid phases rather than the difference in the peak energies.[4c]

In the case of a polymer solid, each chain corresponds to a molecule in the above discussion. Thus, the discussion regarding a photoelectron spectrum of a polymer solid can be divided into that of (1) the electronic structure of an isolated chain and (2) the polarization energy. The character of the occupied orbitals and their relative energy difference is determined by the former factor, while both factors affect the absolute energy scale.

Figure. 6 illustrates our way of interpreting the observed thresholds and spectral features. At first we

TABLE 1. THE THRESHOLD IONIZATION ENERGIES OF VINYL POLYMERS (I_s^{th}) AND THE GAS PHASE THRESHOLD IONIZATION ENERGIES OF THEIR "UNIT" COMPOUNDS (I_g^a)

Compound	I_s^{th}/eV	Assignment	Unit compound	I_g^a (unit)/eV	ΔI/eV[g]
PE	8.5[a]	backbone	CH_3CH_3	11.7[c]	3.2
PP	8.5	backbone	$CH_3CH_2CH_3$	11.1[c]	2.6
PVF	9.2	backbone	CH_3CH_2F	11.7[d]	2.5
1,2-PBD	7.5	pendant	$CH_3CH_2CH=CH_2$	9.7[e]	2.2
PVC	8.8	pendant n_{Cl}	CH_3CH_2Cl	11.0[c]	2.2
PVA	8.0	pendant n_O	CH_3CH_2OH	10.3[c]	2.3
PS	6.9_5[b]	pendant	$CH_3CH_2C_6H_5$	8.6[f]	1.7

PP: polypropylene, PVF: poly(vinyl fluoride), 1,2-PBD: 1,2-polybutadiene, PVC: poly(vinyl chloride), PVA: poly(vinyl alcohol), PE: polyethylene, PS: polystyrene.
a) Ref. 7a). b) Ref. 5a). c) Ref. 21a). d) Ref. 16. e) Ref. 17. f) Ref. 18. g) $\Delta I \equiv I_g^a(\text{unit}) - I_s^{th}$.

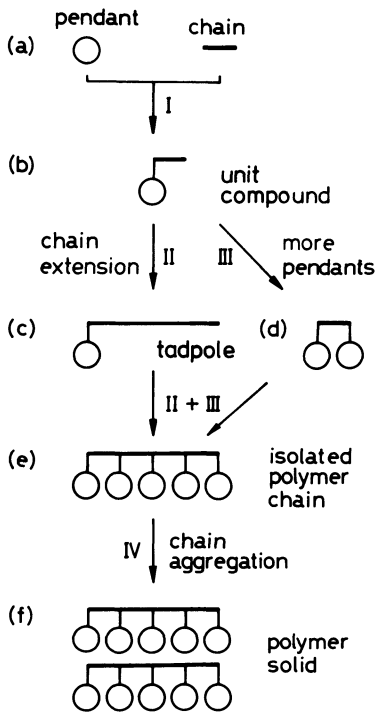

Fig. 6. Schematic representation of the evolution of the electronic structure of a vinyl polymer solid from those of small units.

estimate the electronic structure of an isolated polymer chain (e) from data for small related molecules, by analyzing the effects of the following steps.

(I) The combination of a pendant with a short alkane C_2H_6 to form a unit compound CH_3CH_2X, which is the repeating unit of a vinyl polymer.

(II) The extension of an alkyl chain to form a "tadpole" compound $CH_3(CH_2)_\infty X$.

(III) The attachment of other pendants to the chain to form an isolated polymer chain.

The remaining difference between the estimated structure of an isolated chain and the observed results for a polymer solid (f) is ascribed to the effect of

(IV) aggregation of chains to form a polymer solid.

Steps (I) and (II) jointly correspond to the interaction of a pendant and the principal (backbone) chain, (III) to the interaction among pendants through space or through the principal chain, and (IV) to the interaction among chains. For small compounds from (a) to (d) in Fig. 6, gas-phase UPS spectra are available. Further, additional information on the isolated polymer chain (e) and polymer solid (f) are available from theoretical band calculations[10-13] and XPS spectra,[10] respectively.

In this analysis, we distinguish the ionization energies for the onset and peak of a band in a photoelectron spectrum. In the gas phase, the peak energy for the ionization from a MO corresponds to ionization without a change in the molecular geometry, while the onset corresponds to the ionization to a relaxed molecular geometry.[20] When we assume Koopmans' theorem, the former corresponds to the orbital energy of the MO.[20] Thus, peak energies are more suitable for discussing the evolution of the electronic structure of a molecule. However, bands originating from different MO's often overlap and no clear peak can be observed, as in some of the compounds studied here. In such cases, we can still discuss the change in the electronic structure using onset energies, assuming that the onset-peak energy separation changes little among similar molecules. In the solid spectrum, on the other hand, the physical meaning of the peak energy is ambiguous owing to various mechanisms of peak broadening.[4b,c] Further, no clear peak can be observed for some of the polymers studied here. Fortunately, however, the polarization energy is obtained as the difference between the thresholds of gas and solid states, as described above. Thus, we don't need the peak energies in order to evaluate the intermolecular effects.

Taking account of such a situation, we will mainly use the onset energies in the following analysis, but will also use peak energies when they are available and useful. We denote the threshold (adiabatic) ionization energies of a tadpole compound and a polymer chain as I_g^a(tadpole) and I_g^a(polymer), respectively. As materials for discussion, Table 2 lists the data[21] for small alkanes with corresponding pendants, *i.e.* the ionization energies of the highest occupied orbitals among (1) orbitals localized on the pendant (I_1), and (2) orbitals delocalized over the chain (I_2).

Electronic Structure of an Isolated Chain. A difficulty in the analysis of step (I) for the small pendants studied here is the choice of a compound embodying the "pendant" X. For larger pendants such as aromatic ones, the attchment of an H atom to X has little effect on the electronic structure of the molecular orbitals, and HX is a natural choice. For small X, however, an H atom strongly affects the electronic structure of HX. Therefore, we will not discuss process (I) in detail and will start from CH_3CH_2X, although we also list the threshold ionization energies of HX[21] in Table 2. This difficulty is the reason why we listed I_g^a(unit)'s in Table 1.

The effect of chain extension (II) can be estimated by examining the dependence of the ionization energies on the carbon number n. As shown in Fig. 7, the ionization potentials of normal alkanes form a good linear relation with $1/n$. The decrease of I_2 with n is due to the delocalization of the highest σ orbital. Also the first vertical ionization energies of alkyl alcohols from C_2H_5OH ($1/n$=0.5) to n-$C_8H_{15}OH$ ($1/n$=0.125)[21i] are also linear with $1/n$ within 0.03 eV. This corresponds to a change of the inductive effect to the O_{2p} lone pair orbital. These empirical relations suggest that we can estimate the threshold ionization energy of a tadpole compound by extrapolation to $1/n$=0 with a probable error of ≈0.1 eV. Such plots are shown by

TABLE 2. IONIZATION ENERGIES OF ONSETS OF ORBITALS LOCALIZED ON PENDANT GROUP (I_1) AND DUE TO PRINCIPAL CHAIN (OR CHAIN-PENDANT BOND) (I_2) OF SUBSTITUTED ALKANES

-X		HX	CH_3CH_2X	CH_3CH_2-CH_2X	CH_3CHX-CH_3	$CH_3CH_2CH_2$-CH_2X	CH_2XCH_2-X	CH_2XCH_2-CH_2X
-H	I_2/eV	15.43[a]	11.65[a]	11.07[a]	11.07[a]	10.63[a]	11.65[a]	11.07[a]
$-CH_3$	I_2/eV	12.98[a]	11.07[a]	10.63[a]	10.55[b]	10.35[a]	10.63[a]	10.35[a]
-F	I_1/eV	16.05[c]	15.3[d]	14.7[d]	—	—	—	—
	I_2/eV	—	11.7[d]	11.3[d]	—	—	—	—
$-CH=CH_2$	I_1/eV	10.51[d]	9.7[e]	9.4[f]	9.5[g]	9.4[f]	9.3[h]	9.1[h]
	I_2/eV	—	11.3[e]	10.8[f]	—	10.6[f]	10.7[h]	10.7[h]
-Cl	I_1/eV	12.75[d]	11.0[d]	10.7[d]	10.7[d]	10.6[d]	11.1[i]	10.9[i]
	I_2/eV	—	12.5[d]	11.8[d]	12.1[d]	11.4[d]	13.1[i]	12.3[i]
-OH	I_1/eV	12.62[d]	10.3[d]	10.1[d]	10.0[d]	10.0[i]	10.3[d]	9.9
	I_2/eV	—	11.6[d]	11.3[d]	11.0[d]	11.0[i]	11.8[d]	11.4
$-C_6H_5$	I_1/eV	9.25[d]	8.6[j]	8.6[j]	8.6[j]	8.6[j]	8.7[k]	—
	I_2/eV	—	10.8[j]	10.7[j]	10.7[j]	10.4[j]	10.7[k]	—

a—j) Ref. 21. Values were read from reported photoelectron spectra unless an explicit value was given in the reference.

TABLE 3. IONIZATION ENERGIES OF NORMAL ALKANES, METHYL SUBSTITUTED ALKANES, AND CYCLOALKANES

[Normal] Compound	I_2/eV	[Branched] Compound	I_2/eV
$CH_3CH_2CH_3$	11.07[a]	CH_3CHCH_3 (CH$_3$ on C2)	10.55[b]
$CH_3CH_2CH_2CH_3$	10.63[a]	$CH_3CHCH_2CH_3$ (CH$_3$ on C2)	10.30[b]
$CH_3(CH_2)_3CH_3$	10.35[a]	$CH_3CHCH_2CH_2CH_3$ (CH$_3$ on C2)	10.09[b]
cyclohexane	9.88[c]	methylcyclohexane	9.86[b]

a) Ref. 21a). b) Ref. 21b). c) Ref. 22.

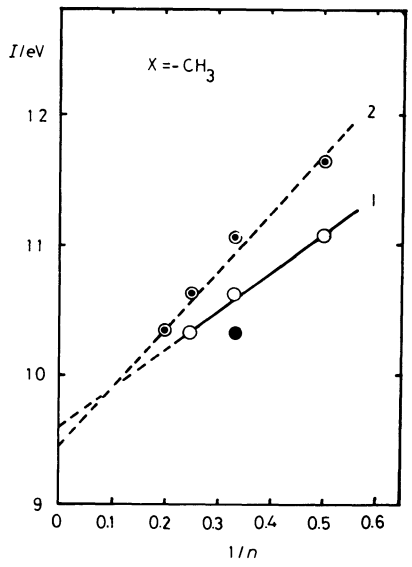

Fig. 7. Dependence of the ionization potential I_2 of normal alkanes (2, ⊙) and their methyl-substituted derivatives (1, ○) on the reciprocal of the chain carbon number n. The value of 1,3-disubstituted propane is also shown (●).

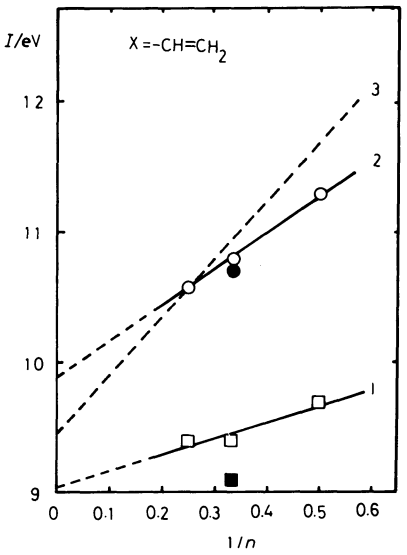

Fig. 8. Dependence of onset ionization energy I of monovinyl-substituted n-alkanes on the reciprocal of the chain carbon number n. 1: onset of π ionization (I_1, □), 2: onset of principal chain ionization (I_2, ○), and 3: I of unsubstituted alkanes from Fig. 7 as a reference. Values of I_1 (■) and I_2 (●) of 1,3-disubstituted propane are also shown.

real lines 1 in Figs. 7—10 for X=CH_3, $-CH=CH_2$, -Cl, and -OH, respectively. The plot for X=F was impossible owing to a lack of data. By assuming a linear relation between I_2 and $1/n$ also, we see that there will be no crossover between I_1 and I_2 in a tadpole compound, with X=Cl being a case that is a little ambiguous.

The further introduction of pendants will affect the electronic structure through (1) the inductive effect and (2) the interaction among pendants. The details of these effects depend on the polymers, so we will now discuss each polymer.

Polyethylene (PE) and Polypropylene (PP): There are

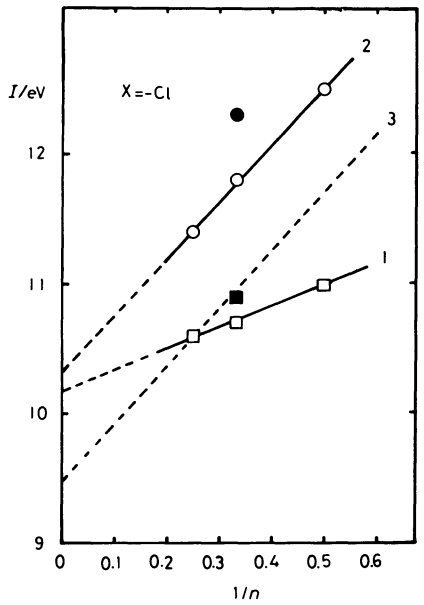

Fig. 9. Dependence of onset ionization potential I of monochloro-substituted normal alkane on the reciprocal of the chain carbon number n. 1: Cl_{3p} ionization (I_1, □), 2: principal chain ionization (I_2, ○), 3: I of unsubstituted alkanes as a reference. Values of I_1 (■) and I_2 (●) of 1,3-disubstituted propane are also shown.

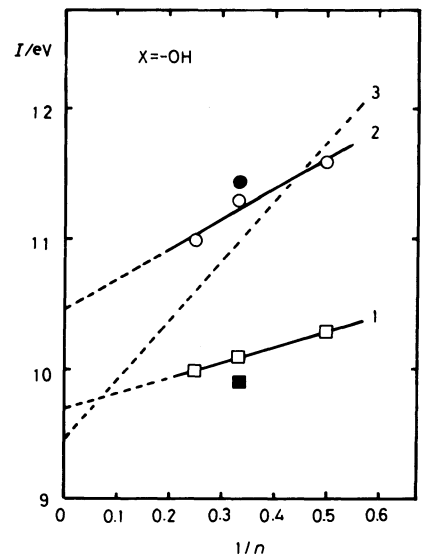

Fig. 10. Dependence of onset ionization potential I of monohydroxy-substituted normal alkanes on the reciprocal of the chain carbon number n. 1: O_{2p} ionization (I_1, □), 2: principal chain or C-O bond ionization (I_2, ○), 3: I of unsubstituted n-alkanes (----) as a reference. Values of I_1 (■) and I_2 (●) 1,3-disubstituted propane are also shown.

only σ-electrons in these polymers, and orbitals are delocalized over the principal chain.

Table 3 lists the I_2's of methyl-substituted alkanes. The values of monomethyl-substituted alkanes are also shown in Fig. 7 (○). The latter are lower than those of unsubstituted compounds (⊙), but the difference decreases with the increase in n and becomes almost zero for $n\rightarrow\infty$. Although the introduction of a second CH_3 group lowers the I_2 for $n=3$ (●) a little, band calculations of isolated chains of PE and PP give a negligible difference between the orbital energies of the HOMOs.[13] Such an insensitivity to the CH_3 substitution can be understood when we consider that (1) the attachment of a CH_3 group does not affect the range of delocalization of the HOMO on the whole chain, and (2) the CH_3 group has almost no inductive effect to alkyl chain.

Therefore, we can expect the I_g^a(polymer) of PP to be the same as I_g^a(tadpole). The latter can be estimated to be 9.6 eV from the extrapolation in Fig. 7 to $1/n=0$. A similar extrapolation for PE gives I_g^a(polymer)=9.4 eV, which is indeed similar to that of PP.

Poly(vinyl fluoride) (PVF): Band calculations[10-12] and XPS[10] show that F_{2p} orbitals have higher ionization potentials than σ orbitals derived from atomic orbitals of carbon and hydrogen. This tendency has already been seen for compounds listed in Table 2. The increase in the length of the alkyl chain seems not to change this situation because of the large difference between I_1 and I_2. Thus, we can expect that the highest occupied orbital is a delocalized one over the principal chain as in the case of PE and PP. The ionization potential of fluoroalkanes in Table 2 are higher than those of corresponding alkanes due to the inductive effect of the fluorine atom. Thus, we expect a higher I_g^a(polymer) of PVF than those of PE or PP. Unfortunately, the data of small related compounds are not sufficient for making a quantitative estimation of I_g^a(polymer).

1,2-Polybutadiene (1,2-PBD): For this polymer, there is a double bond in the side chain with π electrons localized in it. It determines the value of I_1. The right-hand peak in the spectrum for $h\nu$=10.33 eV (Fig. 3) should correspond to this orbital, since such a distinct peak does not appear in the spectra of PE.[7a]

The effect of introducing more than one vinyl group can be seen in $CH_2=CH(CH_2)_3CH=CH_2$ (■, ● in Fig. 8) in which the number of carbon atoms between the pendants is the same as in the polymer. As seen from the vertical ionization energies listed in Table 4, the interaction of the two vinyl groups results in a splitting of 0.4 eV between the π ionization energies of $CH_2=CH(CH_2)_3CH=CH_2$, while their centroid does not shift from the π ionization energy of $CH_3(CH_2)_2CH=CH_2$. This means that the inductive effect of the vinyl group is small, and only the π-π interaction is important. The change of I_2 by the inductive effect is also very small. As a result, I_1 is more decreased than I_2 and the I_g^a(polymer) is determined by the π orbitals.

The effect of π-π interaction in an isolated infinite polymer chain can be evaluated by a simple theory of a one-dimensional chain with only the nearest-neighbor

TABLE 4. VERTICAL IONIZATION ENERGIES OF $CH_3CH_2CH_2X$ AND $XCH_2CH_2CH_2X$ (IN eV)

X	CH_3CH_2CHX I_0	$XCH_2CH_2CH_2X$ I_I	I_{II}	Splitting $I_{II}-I_I$	Shift $(I_I+I_{II})/2-I_0$
$CH=CH_2$	9.7_0[a]	9.5_2[b]	9.9_3[b]	0.4_1	0.0_3
Cl	10.8_8[c]	11.1_6[d]	11.5_5[d]	0.3_9	0.4_8
OH	10.4_9[c]	10.2_4[e]	10.9_0[e]	0.6_6	0.0_8

a) Ref. 20f). b) Ref. 20h). c) Ref. 16. d) Ref. 20i). e) Present results.

interaction β among the units. According to this formalism, the splitting for a dimer is 2β and the energy spread for an infinite chain is 4β, which is symmetric with respect to the energy of one unit.[23] Therefore, the lowest ionization potential in the infinite chain should be lower than that of one unit by the amount of the splitting in the dimer. Assuming the same amount of decrease in the threshold ionization energy as that in the peak energy, we can expect that the value of I_g^a (polymer) is 0.4 eV smaller than I_g^a(tadpole), which can be estimated to be 9.1 eV from the extrapolation in Fig. 8. This gives I_g^a(polymer)=8.7 eV.

Poly(vinyl chloride) (PVC): The values of I_1 are determined by the two Cl_{3p} lone pairs. In the He I spectrum, three features at E_k=11.0, 9.0, and 6.5 eV (I_s=10.2, 12.2, and 14.7 eV) can be clearly seen. These features were also observed in the reported XPS spectrum,[10] with a good agreement of intervals. They should be due to the Cl atoms.

The effect of multiple Cl-substitution can be examined as in the case of 1,2-PBD using the ionization potentials in Table 4. Similar to 1,2-PBD, the introduction of the second Cl atom in $CH_3CH_2CH_2Cl$ gives a splitting of 0.4 eV in the Cl_{3p} lone-pair bands. Unlike 1,2-PBD, however, the large inductive effect of the Cl atoms raises the centroid of these bands by 0.5 eV from that of $CH_3CH_2CH_2Cl$. As a net result of these conflicting effects, I_1 is even increased by 0.3 eV (■ in Fig. 9). On the other hand, I_2(●) experiences only an inductive effect, and is significantly increased (≈0.5 eV).

With the simple theory described for 1,2-PBD, the interaction among the lone pairs in an infinite PVC chain will lower the Cl_{3p} ionization energy by 0.4 eV relative to that of $CH_3(CH_2)_\infty Cl$. The inductive effect will not change the centroid of the Cl 3p levels significantly from that in $Cl(CH_2)_3Cl$ by further Cl-introduction, judging from the small change of ionization energy from CH_2ClCH_2Cl (11.41 eV)[16] to $CHCl_2CH_2Cl$ (11.48 eV)[16] and CCl_3CH_2Cl (11.45 eV).[16] With these conflicting effects, we expect that I_1 will change only a little (≈0.1 eV increase) from $CH_3(CH_2)_\infty Cl$ to $\{CH_2CHCl\}_n$. The value of I_2 will be increased by an inductive effect. With these values and the extrapolation of the lines in Fig. 9 to $1/n=0$, we see that the HOMO of the polymer is derived from the Cl_{3p} lone-pair orbitals with I_g^a(polymer)≈I_g^a(tadpole)= 10.3 eV. The peak at I_s=10.2 eV in Fig. 4 should correspond to this. This assignment agrees with that from XPS.[10] For deeper levels, contributions from lone pairs, C–Cl bonds, and alkyl chains overlap and form peaks of I_s=12.2 eV and 14.7 eV. Since these peaks do not appear in the spectrum of PE, we will tentatively follow the assignments by Pireaux *et al.*[10] to lone pair and C–Cl bonds, respectively.

Poly(vinyl alcohol) (PVA): There are two O_{2p} lone pairs per oxygen atom, which determine the value of I_1.

The way of discussing the effect of the multiple introduction of OH groups is the same as those for 1,2-PBD and PVC, but we must pay attention to the effect of possible hydrogen bonding.[24] Such hydrogen bonding should lead to a larger interaction than the usual van der Waals interaction. As for the intramolecular hydrogen bond, the data of $HO(CH_2)_3OH$ in Table 4 indeed gives a large splitting of 0.6_6 eV for orbitals. The inductive effect of the new OH group is small (0.1 eV increase) for both the mean ionization energy of such a split pair and I_2 (Table 4). With a similar discussion as for 1,2-PBD and PVC, we can estimate a decrease of I_1 by 0.6 eV from $CH_3(CH_2)_\infty OH$ to $\{CH_2CHOH\}_n$.

In the case of an intermolecular hydrogen bond, the inductive effect by the OH groups in the same chain will remain small, but the intramolecular O_{2p}–O_{2p} interaction should be smaller than for the case of an intramolecular hydrogen bond. Instead, the intermolecular interaction of OH groups should cause a lowering of the ionization potential comparable to that from methanol (10.96 eV) to methanol dimer (10.42 eV).[25] Although this is not an intramolecular effect, the total difference between I_g^a (tadpole) and I_s^h should be similar to that in the case of an intramolecular hydrogen bond.

In any case, the ordering of I_1 and I_2 in a polymer chain is not changed from that in $CH_3(CH_2)_\infty OH$ estimated by the extrapolation in Fig. 10, and O_{2p} lone pairs will form the HOMO. Pireaux *et al.*[10] made the same assignment from XPS. The estimated value of I_g^a (tadpole)=9.7 eV gives I_g^a (polymer)=9.1 eV for a polymer chain with intramolecular hydrogen bonds.

Polystyrene (PS): As seen above, the highest occupied states of 1,2-PBD, PVC, and PVA are rather localized on a pendant group, in contrast to the case of PP and PVF where the highest occupied orbital is delocalized over the principal chain. A hole in the cationic state of

aromatic-pendant vinyl polymers is also known to be localized in a pendant group.[5] Therefore it is interesting to compare the present results described above with those of aromatic-pendant polymers.

We will examine polystyrene (PS) as a typical example. In PS, the highest occupied orbital gives a much smaller ionization energy (I_1) than that of the principal chain (I_2), as in most other aromatic-pendant polymers. Further, I_1 does not depend on the length of alkyl chain as shown in Fig. 11. Similar insensitivity to the size of alkyl group can be also seen in the small difference between *N*-ethylcarbazole and *N*-isopropylcarbozole.[26] Such an independence of the chain length is different from the tendency observed for the polymers studied above. This small interaction should be a result of the large difference in energy between π and σ orbitals and the small difference in electronegativity between the chain and the pendant. Another difference is an almost negligible interaction between the aromatic rings as seen in the small difference of I_1 values for ethylbenzene and bibenzyl in Table 2.

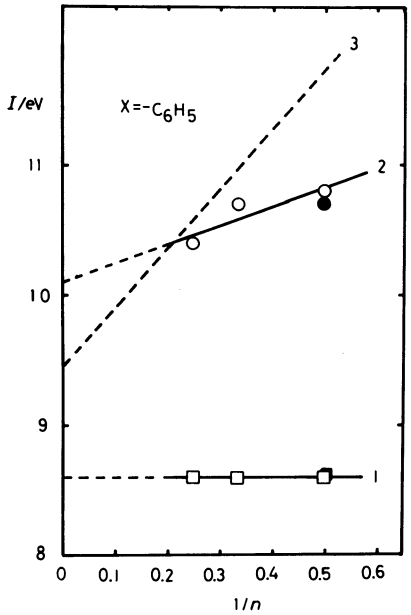

Fig. 11. Dependence of onset ionization potential I of monophenyl-substituted normal alkanes on the reciprocal of the chain carbon number n. 1: π ionization (I_1, □), 2: σ ionization (I_2, ○), 3: I of unsubstituted n-alkanes as a reference. Values of I_1 (■) and I_2 (●) of 1,2-disubstituted ethane are also shown.

The value of I_s^{th} is thus determined almost solely by a pendant phenyl group. In this sense, the picture of the ionization of one chromophore is more adequate in the aromatic-pendant polymers than in the other polymers studied here. As a result, both I_g^a(tadpole) and I_g^a(polymer) are expected to be the same as the threshold of ethylbenzene (8.6 eV).

Polarization Energies. Table 5 lists the estimated values of I_g^a(tadpole), I_g^a(polymer), and the polarization energy as the difference I_g^a(polymer)$-I_s^{th}$. It also lists the refractive indices n_D[29] as a guide for the polarizability. Possible errors of P is ±0.3 eV for PE, PP, and PS, while those for 1,2-PBD, PVC, and PVA should be larger (say, ±0.5 eV), mainly due to the uncertainty about the conformational dependence of the pendant-pendant interaction. Thus, we cannot discuss the latter group in detail. We only note that the value of the latter group are within the range covered by those of the former group.

On the average, these values are comparable or a little smaller than the common value of 1.7 eV for aromatic hydrocarbons,[4c] while aliphatic hydrocarbons have similar values. (Although PS has a P=1.7 eV, it is still smaller than the value 2.1 eV for benzene solid[27]). A possible factor contributing to such a trend is the polarizability of the molecules. The refractive indices in Table 5 are comparable to those of aliphatic solids,[27] but smaller than those of aromatic hydrocarbons. (*e,g*, n_D of anthracene for the three optical axes are 1.550, 1.775, and 2.04[30]).

Further, we also note two differences of polymer solids from molecular solids. (1) For some polymers, the positive charge is delocalized in a long chain in contrast to the localization in a molecule. At present there is no satisfactory theoretical method of estimating P for such a case. This situation may contribute to the small P of PE and PP. (2) Even for a localized positive charge, considerable part of the medium surrounding the charge may belong to the same molecule. Thus, the polarization effect from other molecules will be smaller than for molecular

Table 5. Estimated values I_g^a(tadpole), I_g^a(polymer) and P

Polymer	I_g^a(tadpole)/eV	I_g^a(polymer)/eV	P/eV	n_D
Polyethylene	9.4	9.4	0.9	1.545[a]
Polypropylene	9.6	9.6	1.1	1.50[a]
Poly(vinyl fluoride)	—	—	—	1.45[b]
1,2-Polybutadiene	9.1	8.7	1.2	1.51[c]
Poly(vinyl chloride)	10.3	10.3	1.5	1.54—1.55[a]
Poly(vinyl alcohol)	9.7	9.1	1.1	1.49—1.53[a]
Polystyrene	8.6	8.6	1.7	1.59[a]

a—c) Ref. 29.

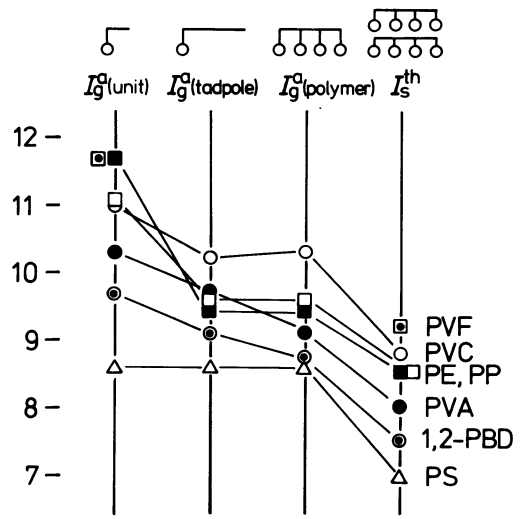

Fig. 12. Change of threshold ionization energy (in eV) from unit compounds to polymer solids.

solids. This may contribute to make the P of PS smaller than for benzene.

Summary of the Evolution of the Electronic Structure. Fugure 12 summarizes the change of threshold ionization energy from the unit compounds to polymer solids. As stated above, the estimated values might not be very accurate, in particular for 1,2-PBD, PVC, and PVA. Nevertheless, Fig. 12 clearly shows how a change of thresholds depends on the class of polymers.

For polymers with the HOMO delocalized over the principal chain, an extention of the chain length decreases the threshold energy effectively by delocalization, as seen in PE and PP. Although we could not make a quantitative examination, compounds related to PVF should also follow this trend. This delocalization is the reason for the larger values of ΔI for PE, PP, and PVF in Table 1 than the other polymers. The introduction of methyl groups into a polymer chain in PP does not affect the thresholds, but we can expect some inductive effect by pendants with a very different electronegativity from carbon, (*e.g.* X=F). Such an inductive effect should be the main reason of the much larger I_s^{th} of PVF than that of PE and PP. Similar large I_s^{th}'s were also found for other fluoropolymers.[31] As seen in Table 5, the polarization energies of these polymers are a little smaller than those of other polymers. It may be partly due to the extended distribution of the positive charge over the chain.

In polymers with aromatic pendants, represented by PS, neither a chain extension beyond CH_3CH_2X nor a pendant-pendant interaction affects the threshold. This fact comes from the well-localized nature of the hole, and makes ΔI smaller than those of the other polymers in Table 1, although the polarization energy is a little larger than for the other polymers.

Other polymers with small nonaromatic pendants (1,2-PBD, PVC, and PVA) show an intermediate behavior between the two classes of compounds described above. A chain extension causes a small decrease in the threshold energy, owing to the inductive effect of the alkyl chain. The introduction of many pendants also results in some change, but its magnitude and sign depend on a balance between the pendant-pendant interaction and the inductive effect.

The above discussion shows that an analysis of the change of ionization energy at the transition from a unit compound to a polymer solid is a fairly complex task. Even the inversion of the order of the threshold energies happens among different polymers. Such a situation is much more complex than for the case of simple molecular solids, where the polarization energy is the only origin of a lowering of the threshold energy from a free molecule. However, as shown above, if the analysis is properly made, it gives a deep insight into the electronic structure of polymers.

We also note that a group of polymers with an intermediate delocalization is new in UPS studies regarding polymers. The polymers so far studied could be classified into two extreme cases where the HOMO is either well delocalized (PE and fully conjugated polymers such as polyacetylene and $(SN)_x$)[8] or well localized (vinyl polymers with aromatic pendants[5] and poly(*p*-phenylene-ethylene,[6] where benzene rings are in the principal chain). The present study shows that the degree of delocalization of the cationic state covers a wide range from almost complete localization to extensive delocalization.

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