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Infrared spectroscopic study and *ab initio* calculation for dissociation of poly(α-hydroxy acrylic acid) in aqueous solutions

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Intramolecular lactone ring formation of poly(α-hydroxy acrylic acid) (PHA) has been investigated as a function of pH with i.r. spectroscopy. I.r. peaks observed at $1772 \pm 14\,\mathrm{cm}^{-1}$, $1724 \pm 4\,\mathrm{cm}^{-1}$, and $1605 \pm 10\,\mathrm{cm}^{-1}$ were assigned to C=O(lactone ring), C=O(COOH), and COO^-, respectively. These i.r. peaks shifted to higher wavenumbers with decreasing pH. This shift was attributed to intramolecular hydrogen bonding, formation of lactone ring, and also to protonation of carboxyl group on the basis of frequency analysis by *ab initio* calculation. The respective molar fractions of lactone, COOH and COO^- groups were estimated as a function of solution pH on the basis of the respective i.r. peak heights. According to the estimation, the fraction of lactone increases with decreasing pH, finally to *ca.* 65 mol% at pH 1. *Ab initio* calculation of the lactone ring formation energy supported the i.r. estimate. © 1997 Elsevier Science Ltd.

(Keywords: poly(α-hydroxy acrylic acid); dissociation behaviour; lactone ring)

INTRODUCTION

A great number of theoretical and experimental studies have been performed to elucidate physicochemical properties of polyelectrolytes in solutions, e.g., conformation[1–3], dissociation of polyacids and polybases[4–8], and counterion condensation[9–14]. Dissociation behaviour of weak polyacids, or polycarboxylates, in particular has received researchers' attention because of the complexity resulting from the intramolecular hydrogen bonding[15,16] and also from counterion binding or electrostatic interaction among charged groups[17–20]. Recent studies have demonstrated that u.v. and i.r. spectroscopy can provide valuable and quantitative information about the state of carboxyl groups during the pH titration[21–23]. By employing these methods, Kawaguchi *et al.*[21,22] have shown that intramolecular hydrogen bonds are formed between COOH and COO^- of some polyelectrolytes carrying maleic acid units, and that this type of hydrogen bond can be formed only when the nearest neighbouring COOH and COO^- lies on the same plane. In addition, it has also been confirmed that poly(itaconic acid) can form hydrogen bond, only when the carboxyl groups are in *gauche* position[23].

Poly(α-hydroxy acrylic acid) (PHA) may be another interesting object for dissociation study, because the polymer may form lactone rings between an unionized carboxyl group and a neighbouring hydroxyl group; the latter also enhances the binding strength for multivalent counterions. This unique polyelectrolyte has found an industrial application as an efficient stabilizer of hydrogen peroxide, which is destroyed in the presence of transition metal cations. However, little is known about basic physicochemical properties of PHA in solution.

Here, we examine the dissociation and cyclization, i.e. formation of lactone ring, behaviour of PHA as a function of solution pH by employing i.r. spectroscopy. We observed that its i.r. peak for COO^-, C=O(COOH) and C=O(lactone ring) shifts with a change of pH, and that the content of lactone rings reaches *ca.* 65 mol% at pH 1. These results are combined with *ab initio* calculations for the lactone ring formation.

EXPERIMENTAL

PHA ($MW = 87\,000$) was kindly supplied as an aqueous solution of the sodium salt at pH 9.6 by Nippon Peroxide Co., Ltd. Poly(acrylic acid) ($MW = 90\,000$) as an aqueous solution was purchased from Polysciences Inc.

The i.r. spectra were obtained on a Shimazu FT-IR 8200PC spectrometer at 25°C. We selected three bands as characteristic absorptions for PHA: stretching vibration of C=O in COOH and lactone ring and asymmetric stretching vibration of COO^-. Because these absorptions appear in a region from 1500 to $1900\,\mathrm{cm}^{-1}$, where ordinary water also shows a strong absorption, deuterated water was used for i.r. measurements. The freeze-dried samples of PHA and PAA were dissolved in D_2O, and HCl or NaOH were added to adjust the polymer concentration, C_p, to 15 wt% and to change the pH values. The solutions were held between two silicon plates separated by a spacer of thin lead film (thickness

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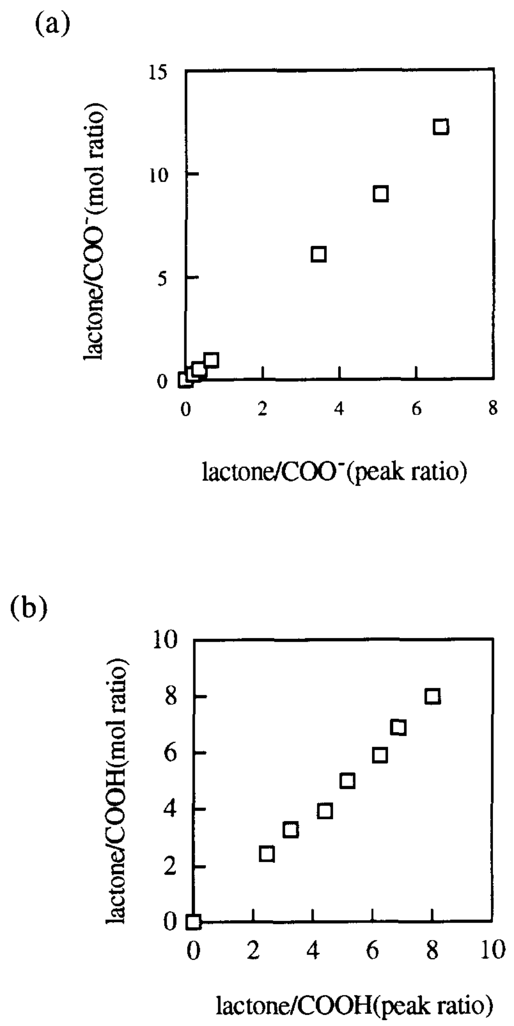

Figure 1 Calibration curves between the molar ratio and the peak ratio. (a) Lactone and COO^-, (b) lactone and COOH

$10\,\mu m$). The sample pH was measured with an F-8 pH meter (Horiba Seisakusho Co., Ltd.). The recording and sample conditions are as follows; resolution, $4.0\,\mathrm{cm}^{-1}$; accumulation, 40 scans; PHA $C_p = 1.36\,\mathrm{N}$, C_s (salt concentration as produced by HCl addition) $= 0 \sim 2.0\,\mathrm{N}$; PAA $C_p = 2.08\,\mathrm{N}$, C_s (as NaOH) $= 0 \sim 1.6\,\mathrm{N}$.

The molar fractions of the three states of the carboxyl groups were estimated on the basis of respective i.r. peak heights; we prepared calibration curves by using the freeze-dried sample of PAA and PHANa, and γ-butyrolactone (Tokyo Kasei Co., Ltd) as reference substances for C=O(COOH), COO^-, and C=O(lactone ring), respectively. The calibration curves for mol ratio *versus* peak ratio were obtained between C=O(COOH) and C=O (lactone ring), and COO^- and C=O(lactone ring), as shown in *Figure 1*. The relation of C=O (COOH) and COO^- was obtained by assuming the two curves as linear.

For *ab initio* calculations, we used the Gaussian 94 program package on Cray C916/12256. Dimer and tetramer models for PHA were optimized with HF/3-21G level. The frequency analysis was performed by using the optimized structure. Tetramer models for PHA were calculated by assuming a syndiotactic configuration.

RESULTS AND DISCUSSION

Peak shift and ab initio *calculation*

The i.r. spectra of PHA and PAA in D_2O at various pH are shown in *Figure 2*. For PAA, i.r. peaks observed at $1705 \pm 2\,\mathrm{cm}^{-1}$ and $1566\,\mathrm{cm}^{-1}$ are assigned to stretching vibration of C=O(COOH) and asymmetric vibration of COO^-, respectively. These analyses are consistent with the results of Kawaguchi *et al.*[21] who observed the two bands at $1705 \pm 3\,\mathrm{cm}^{-1}$ and $1567 \pm 1\,\mathrm{cm}^{-1}$, respectively. For PHA, i.r. peaks observed at $1772 \pm 14\,\mathrm{cm}^{-1}$, $1724 \pm 4\,\mathrm{cm}^{-1}$, and $1605 \pm 10\,\mathrm{cm}^{-1}$ appear to correspond to the stretching vibration of C=O(lactone ring), stretching vibration of C=O(COOH), and asymmetric stretching vibration of COO^-, respectively. The assignment of C=O(lactone ring) was confirmed by i.r. measurement of γ-butyrolactone, which shows the corresponding i.r. peak around $1745\,\mathrm{cm}^{-1}$. As seen in *Figure 2a*, the wave-numbers of absorption peaks ascribed to C=O(lactone ring), C=O(COOH) and COO^- increase with a decreasing pH. The pH dependencies of the respective peak wave-numbers for the two polymers are plotted in *Figure 3*. For PAA, those of C=O(COOH) and COO^- are approximately constant over the whole pH region. For PHA, however, the peaks of C=O(lactone ring), C=O(COOH), and COO^- shift to a higher wave-number by $27\,\mathrm{cm}^{-1}$, $7\,\mathrm{cm}^{-1}$, and $19\,\mathrm{cm}^{-1}$, respectively, for pH 9.6–pH 0.3. Similar peak shifts have been observed for C=O(COOH) and COO^- of poly(fumaric acid), poly(maleic acid)[22], and poly(itaconic acid)[23]. These have been previously attributed to intramolecular hydrogen bonding. In the present case also, the peak shifts observed for C=O(COOH) and COO^- may be attributed to such intramolecular hydrogen bonding. However, one should note that COOH groups appear only at the lower pH range (<4.0). Therefore, the supposed hydrogen bond donor for COO^- at higher pH range cannot be a COOH group; only the α-OH group may be considered as donor. Thus, we performed *ab initio* calculation for structural optimization. *Figures 4a* and *b* show the distance and angle of the possible hydrogen bond for PHANa and for lactone ring formed by protonation of PHANa. The distance and the angle for PHANa is 1.816 Å and 126.9°, while those for lactone ring are 1.553 Å and 161.4°, respectively. Briefly, the hydrogen bond distance for the latter is shorter and more linear than that for PHANa. These results suggest that the lactone ring formation favours the hydrogen bonding between COO^- and OH. Thus, the displacement in the peak wave-number may be attributed mainly to the increase in the degree of hydrogen bonding. This point will be considered again at the end of this discussion.

In *Figure 4*, the results of frequency analysis with *ab initio* calculation are also shown; the comparison of *Figures 4a* and *b* shows that the peak of COO^- shifts to higher wave-number by $32\,\mathrm{cm}^{-1}$ with lactone ring formation, a result consistent with the experimental observation.

With *Figures 4b* and *c*, one can compare the peak wave-numbers of C=O(lactone ring) for lactone ring in the ionized and acid form. It is seen that C=O(lactone ring) shifts to higher wavenumber by protonation of the carboxyl anions. Further, from *Figures 4d* and *e*, one can see that the peak for C=O(COOH) shifts to higher wavenumber with an increasing F_{lac} when F_{lac} is larger than 50 mol%. All these estimates appear to give a

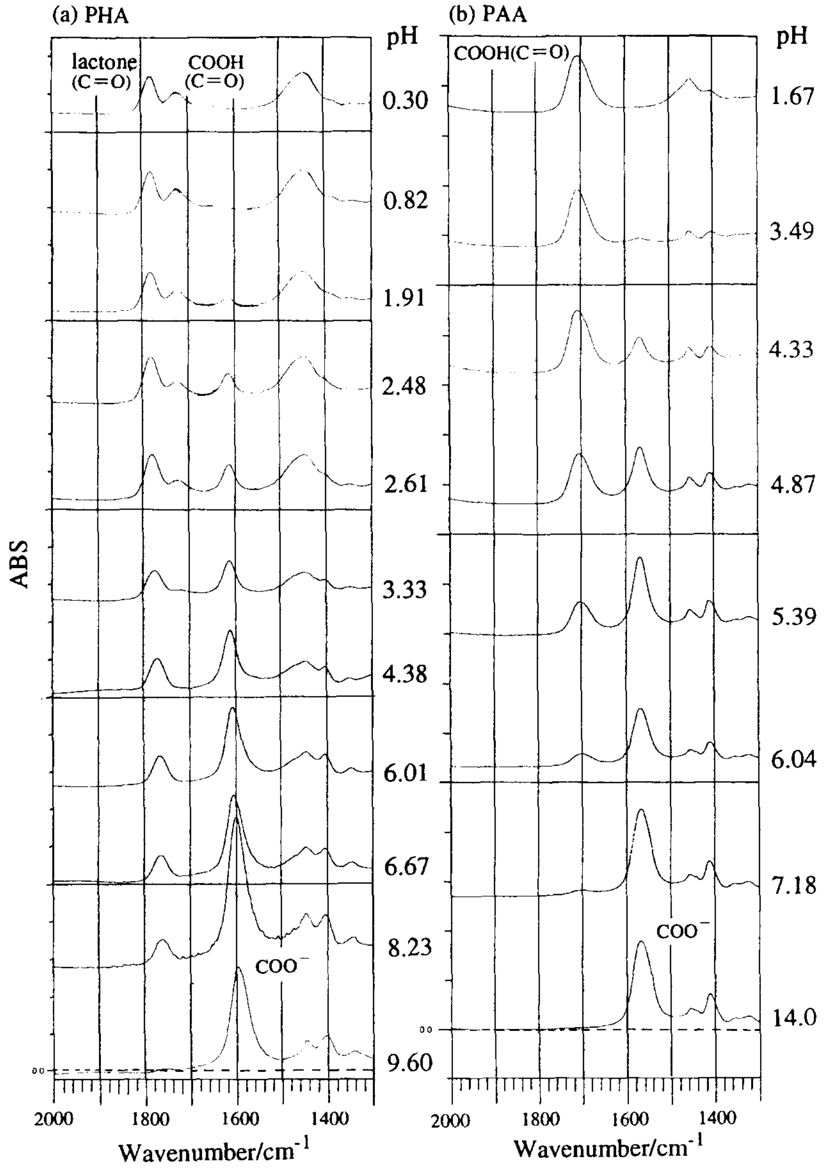

Figure 2 The i.r. spectra at various pH: (a) PHA, $C_p = 1.36$ N, $C_s = 0$–2.0 N; (b) PAA, $C_p = 2.08$ N, $C_s = 0$–1.6 N; resolution 4.0 cm^{-1}, accumulation 40 scans, path length 10 μm

qualitative explanation for the observed i.r. peak shifts.

Quantitative estimation of lactone, COOH and COO$^-$ groups

With the prepared calibration curves (*Figures 1a* and *b*), mol fractions were estimated for COOH, COO$^-$ and lactone ring as a function of pH, which are shown in *Figures 5a* and *b*, and *Table 1*. In the last column of the table, COO$^-$ fraction estimated by pH measurements is given as the degree of dissociation, α. These α values have been estimated by taking into account an experimental observation that PHA contains *ca.* 3 mol% of lactone ring even at pH 9.6 before HCl addition. One can see that the α values thus obtained are compared to the COO$^-$ mol fractions from i.r. measurement to support the present i.r. method for quantitative estimation of carboxyl group fraction in the respective states.

It is seen from comparison of *Figures 5a* and *b* that COO$^-$ mol fraction of PHA is lower than that of PAA at the higher pH range, while the trend is inverted in the lower pH range. The former appears to be consistent with the fact that almost all the protons initially added into the PHANa solution are dissipated to form lactone rings, which means pK_a of PHANa is rather high; in fact at $\alpha = 0.9$, pK_a for PHANa is *ca.* 7.8 while that of PAANa is *ca.* 6.0. However, the inversion of pK_a at the lower pH range (e.g. at $\alpha = 0.1$, pK_a = 2.9 for PHA, 5.0

Table 1 Molar fractions (mol%) of the three states of the carboxyl groups for PHA at various pH and degree of dissociation (α)

pH	F_{lac}	F_{COOH}	F_{COO^-}	α
0.30	64.5	35.5	0	
0.82	63.8	36.2	0	
1.91	61.4	30.1	8.4	0.093
2.48	60.2	23.8	16.0	0.166
2.61	57.9	21.3	20.9	0.199
3.33	51.6	13.9	34.4	0.334
4.38	50.0	0	50.0	0.478
6.01	40.1	0	59.9	0.637
6.67	34.6	0	65.4	0.708
8.23	23.7	0	76.3	0.837
9.60	2.9	0	97.1	0.971

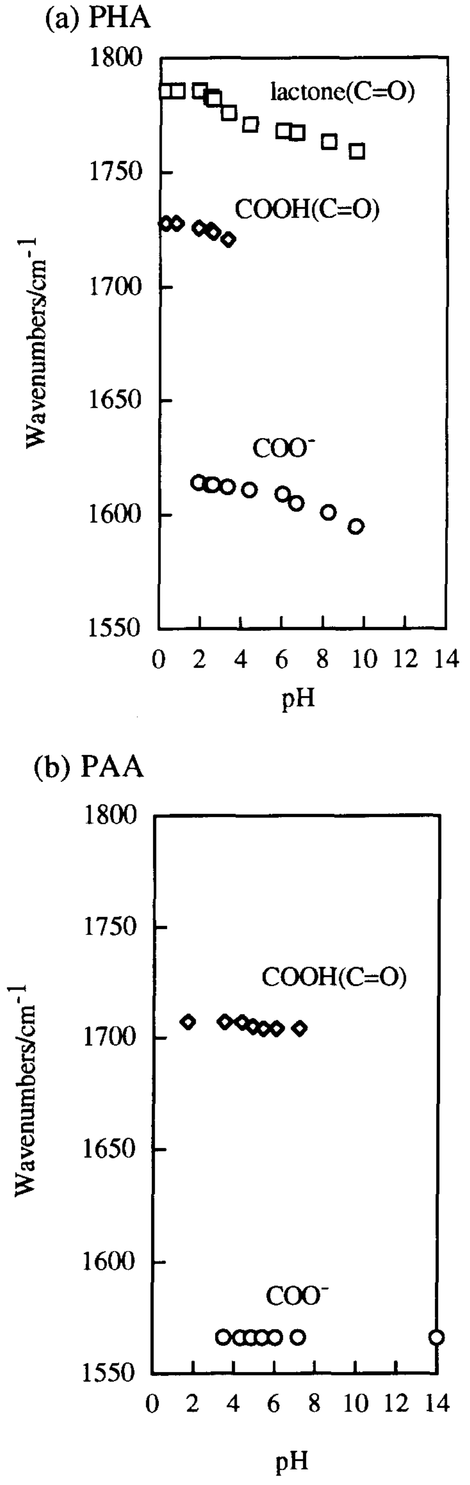

Figure 3 Plots of characteristic absorption wave-numbers against pH. (a) PHA, (b) PAA

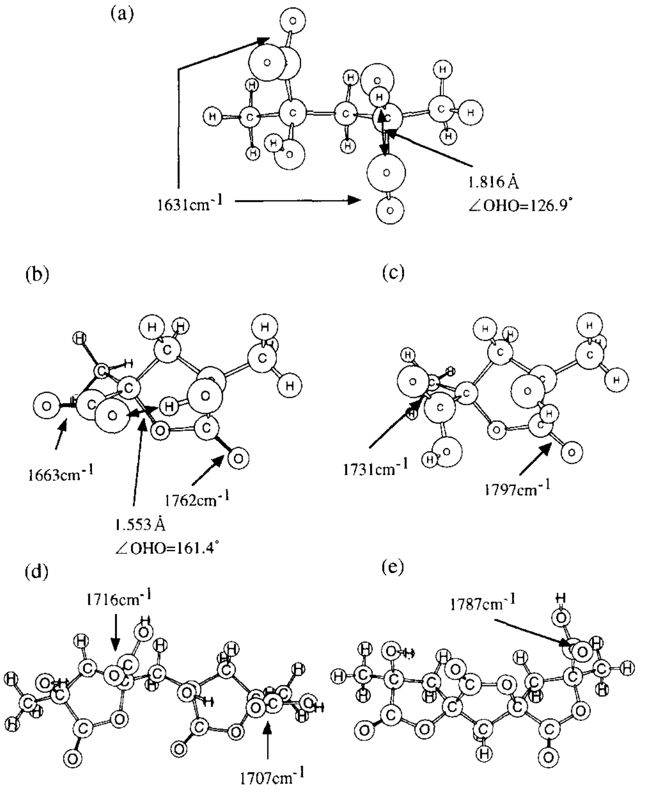

Figure 4 The i.r. peak wave-number estimated by *ab initio* calculation. (a) Dimer of PHA (bond length and angle for the supposed hydrogen bonding between COO^- and OH are also shown). (b) Lactone ring in sodium form (bond length and angle for the supposed hydrogen bonding between COO^- and OH are also shown). (c) Lactone ring in acid form. (d) Two lactone rings. (e) Three lactone rings

for PAA) may be ascribed to the induction effect by α-OH group. For example, lactic acid as a monomer analogue for PHA has a pK_a which is lower by 1.0 than propionic acid (in water at 25°C).

Figure 5a shows that the fraction of lactone increases in two steps with decreasing pH, i.e., one saturation at around 50 mol% and the other at *ca.* 65 mol%. A similar two-step variation has been observed for the peak wave-number of C=O(lactone ring), which may result from the same cause. At 50 mol% lactone content, all residues may take part in lactone formation through OH or COOH groups, when the cyclization takes place at every other residue. If it is the case, the ring formation above 50 mol% takes place for a residue between two adjacent lactone rings, the process may be different in the free energy from that at the lower half lactone ring content. We examined the possibility by *ab initio* calculation. The results are shown in *Figure 6*. The positive reaction energies mean that the respective steps are endothermic reaction. Although the total free energies may become negative because of a concomitant entropic contribution from the H_2O molecule liberated during the reaction, we confine our attention to a qualitative comparison of the estimated reaction energies. The first two cyclization steps, which correspond to $F_{lac} < 50$ mol%, are characterized by comparable energies, while the energy for the last step, corresponding to $F_{lac} > 50$ mol%, is significantly lower. This seems to explain the increase in F_{lac} above 50 mol% despite natural enhancement of the chain stiffness. The second saturation of F_{lac} at 65 mol% may be ascribed to steric hindrance upon the lactone formation and relative stabilization of COO^- groups because of the reduced electrostatic repulsion under the lower pH condition.

Finally, we return to *Figure 3a* and consider the supposed hydrogen bonding between OH and COO^- groups. Here, we note a bend in the plot of COO^- wave-number at pH 6.0. According to the above estimation (*Table 1*), the molar fraction of lactone ring reaches *ca.* 40 mol% at the relevant pH. Since the hydrogen bonding fraction should saturate at $F_{lac} = 50$ mol%, the bend may correspond to the saturation. Then, we may

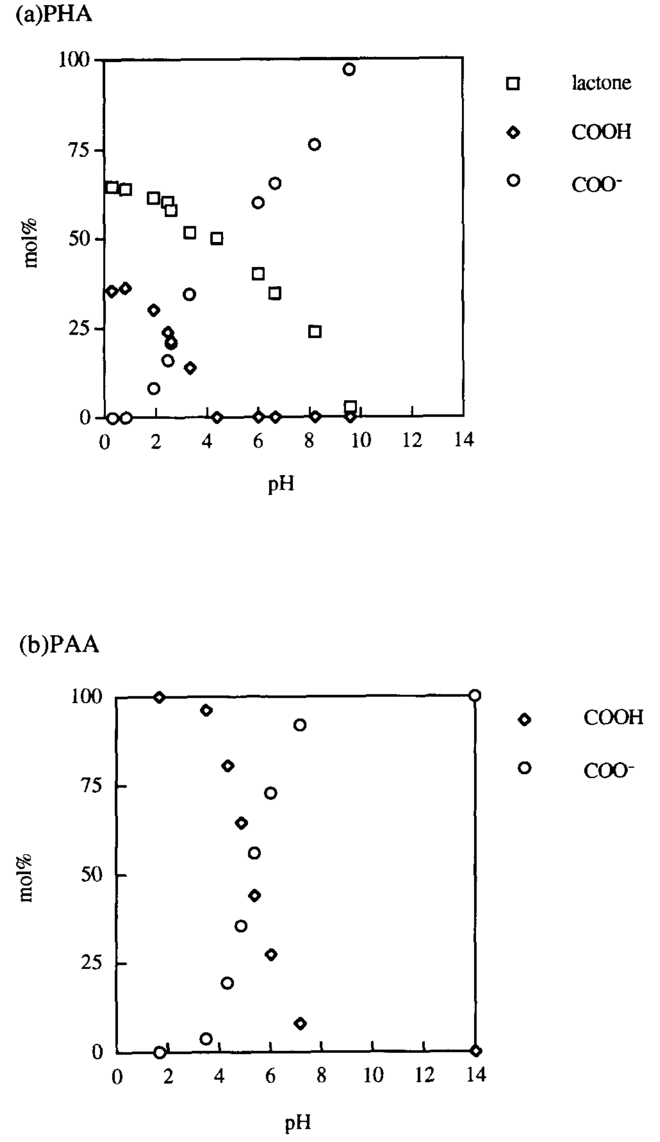

Figure 5 Molar fractions for the respective states of the carboxyl group. (a) PHA, (b) PAA

estimate the hydrogen bonding fraction by spectrum resolution of COO^- peaks between pH 9.6 and 6.0. The respective peaks were divided into two subpeaks that can be represented by Gauss function: one is at 1595 cm^{-1} assigned to free COO^- and the other is at 1612 cm^{-1} for hydrogen bonded COO^-. We obtained a rough estimation of the latter fraction, F_{hyd}, by using the resolved peak heights as; $F_{\mathrm{hyd}} = 0$, 15, 38, and 52 at pH = 9.60, 8.23, 6.67, and 6.01, respectively. The last value should be taken as the upper limit because the peak displacement should contain a contribution from enhanced rigidity of the polymer segment with lactone ring formation, as suggested by the above *ab initio* calculation for COOH (*Figures 4d* and *e*). Thus, the enhancement in the rigidity appears to be responsible also for the gradual peak shift observed for COO^- below pH 6.0.

In conclusion, we have performed a quantitative estimation for the three states of carboxyl group; lactone, COOH and COO^-, on PHA in aqueous solution as a function of pH by employing i.r. spectroscopy with assistance of *ab initio* calculation. These basic experimental data and findings will be utilized in the subsequent studies, for example, on gel formation of PHA by γ-ray irradiation, in which the lactone ring formation plays an essential role.

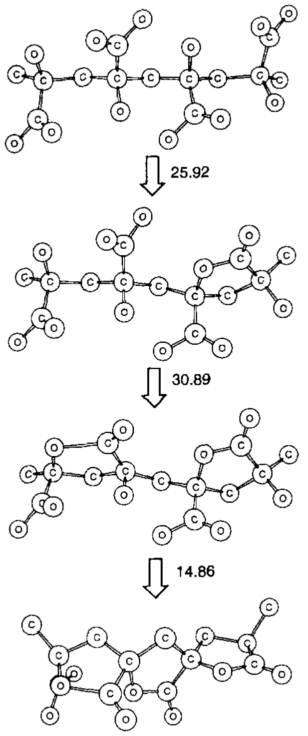

Figure 6 Lactone ring formation energies estimated by *ab initio* calculations (kcal mol^{-1})

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