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Preparation of poly(α-hydroxyacrylic acid) gel by γ-irradiation and its swelling behaviour

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Gels of poly(α-hydroxyacrylic acid) (PHA) and poly(acrylic acid) (PAA) were prepared by gamma irradiation of 15 wt% aqueous solutions. Gelation of the two polymers occurred only in the lower pH range (1–4). *Ab initio* energy calculations for radical formation on the PHA main chain suggested that the hydrogen atom of the hydroxyl group is easily attacked by hydroxyl radicals when a lactone ring is formed between adjacent OH and COOH groups. The swelling ratios (SR) of PHA and PAA gels were measured in water as a function of state of dissociation of the COOH group. For PHA gel, SR gradually increased above pH 1 and steeply above pH 6. The steep increase for PHA is ascribed to lactone ring-opening in the gel, as suggested by i.r. peak displacement. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(α-hydroxyacrylic acid); γ-irradiation; gelation)

INTRODUCTION

Polyelectrolyte hydrogels exhibit remarkable swelling or collapse in response to external stimuli such as pH, salt concentration, solvent composition and temperature[1–5]. They have received much attention for applications such as controlled drug release, separation materials and solvent recovery[6,7].

Poly(α-hydroxyacrylic acid) (PHA) may be an interesting substance for studying the swelling behaviour of the corresponding gel. PHA forms a lactone ring between an un-ionized carboxyl group and a neighbouring hydroxyl group. In our previous study[8], i.r. spectroscopy of PHA in aqueous solution and *ab initio* vibration analysis suggested that the α-OH group forms intramolecular hydrogen bonding with the ionized carboxyl group. However, only a few studies are so far available for PHA, even on fundamental physicochemical properties.

In the present study, we first attempted preparation of PHA gel and found that it is made possible by γ-irradiation of an acidic aqueous solution of PHA. The gelation mechanism was also investigated by *ab initio* calculation. Further, to obtain fundamental data for a forthcoming study on PHA gel collapse, swelling ratios of PHA gel thus prepared were investigated as a function of pH of the pretreatment solution. The correlation between swelling behaviour and lactone ring formation is discussed.

EXPERIMENTAL

Material and gel preparation

PHA (MW = 87 000) was kindly supplied as an aqueous solution of the Na salt by Nippon Peroxide Co. Ltd. Poly(acrylic acid) (MW = 90 000) as an aqueous solution was purchased from Polysciences Inc. These two polymers were used without further purification. Gels were prepared by irradiating 15 wt% aqueous solutions of the polymers with γ-rays (^{60}Co). The pH of the sample solutions was adjusted to 1, 2 and 3 by adding HCl and NaOH. The γ-ray dose was 150, 250 or 300 kGy for PHA, and 50 or 150 kGy for PAA.

Measurement of gelation fraction and swelling ratio

Gels thus prepared were immersed in distilled water for a few days to remove un-cross-linked polymer and low-molecular-weight substances. The gelation fraction (f_g) was calculated as $f_g = 100 \times W_g/W_t$, where W_g and W_t are the amounts of polymer in the gel and before irradiation respectively. The dependence of swelling ratio (SR) on the dissociation state of COOH was examined for gels prepared from pH 2 solution; gels were immersed in solutions of pH 1, 3, 5, 7, 9, 11 (and 13 only for PAA) for one day and then in distilled water for one day. SR was estimated as $\mathrm{SR} = W_w/W_g$, where W_w is the amount of water in the gel. It should be noted that all SR values were obtained for gels immersed in water whose pH was ~5.5.

Infrared spectroscopy

Infrared spectra of PHA gels prepared similarly to those for SR measurement were obtained on a Shimazu FT-i.r. 8200PC spectrometer at 25°C. As characteristic absorptions for PHA, we selected three bands: stretching vibration of C = O in COOH and lactone ring and asymmetric stretching vibration of COO$^-$. Since these absorptions appear in the region 1500–1900 cm^{-1}, where ordinary water also shows a strong absorption, the gels were immersed in deuterated water for i.r. measurements. The fraction of carboxyl groups of the lactone ring was estimated on the basis of the relevant i.r. peak wavenumber. The recording condition was as follows; resolution, 4.0 cm^{-1}; accumulation, 40 scans.

Ab initio calculation

Ab initio calculation was performed using the Gaussian 94 package on a Cray C916/12256 computer. The dimer

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Table 1 Gelation[a] of PHA and PAA in solutions (15 wt%) at different pH values. Dosage: PHA, 150 kGy; PAA, 50 kGy

Sample	pH							
PHA	1.0	2.0	3.0	4.0	6.8	7.8	8.4	9.6
	○	○	○	○	×	×	×	×
PAA	1.0	2.0	3.0	4.0	6.1	13.5		
	○	○	○	○	△	×		

[a] ○, gel; △, viscous fluid; ×, solution

models for PHA and PAA and the monomer models for the lactone ring were used. The structures were optimized with the HF/3-21G level. The symmetry was not considered. The heat of H and OH abstraction by hydroxyl radicals was obtained from the results of the calculations.

RESULTS AND DISCUSSION

pH condition for gel formation and ab initio calculation

Table 1 shows the results of γ-irradiation of PHA and PAA aqueous solutions as a function of solution pH. Gelation was observed only under acidic conditions (pH $\leq$ 4) for both polymers. It should be noted that this is the first time that gelation by γ-irradiation of a polymer which has no α-hydrogen has been reported. It has been known that polymers which have α-hydrogen, such as poly(acrylic acid) and poly(vinyl alcohol), are cross-linked in aqueous solution by γ-irradiation[9,10]. This has been interpreted as easy abstraction of α-hydrogen by hydroxyl radicals produced from the water. However, PHA has no α-hydrogen on the chain. We therefore attempted to examine the cross-linking site of PHA as well as PAA by *ab initio* calculation. The calculations were performed for a dimer model of PHA or PAA and also for a monomer model of lactone, which is a major form of PHA in acidic solution[8]. *Figure 1* shows the heat of H and OH abstraction by hydroxyl radicals produced from the water. For PAA, the negative values for the abstraction from α-carbon, signifying exothermic reaction, suggest that both forms of PAA, namely the COO^- and COOH forms, are able to provide a cross-linking site at the α-carbon. However, this is not fully consistent with the experimental observation that gelation occurs only at lower pH. This apparent discrepancy between the experimental results and *ab initio* calculation at higher pH may be ascribed to another factor which controls the cross-linking reaction. For example, higher charge density of the polymer seems largely to retard the reaction by electrostatic repulsion.

On the other hand, for PHA, the heats of abstraction of OH and H were estimated as positive, suggesting an endothermic or unfavorable reaction. Then we tested the lactone ring, a major conformation of PHA at lower pH. As shown in *Figure 1(f)*, *ab initio* calculation suggested that cross-linking sites can be produced on the chain by abstraction of H of the hydroxyl group on the lactone ring. These results are consistent with the experimental results that gelation was observed only at lower pH.

Fraction of gelation

Values of f_g were obtained for PHA and PAA gels prepared by γ-irradiation of 300 or 150 kGy and 150 or 50 kGy respectively. The relation between f_g and pH of the sample solution for γ-irradiation is shown in *Figure 2*. Here we consider three kinds of effect on f_g: dose, polymer species and pH. The first enhanced f_g, as expected. For the second, f_g of PAA was higher than that of PHA in spite of the lower dose for PAA. This result shows that gelation of PAA or cross-linking reaction proceeds much more easily than for PHA. One possible reason is the difference in the

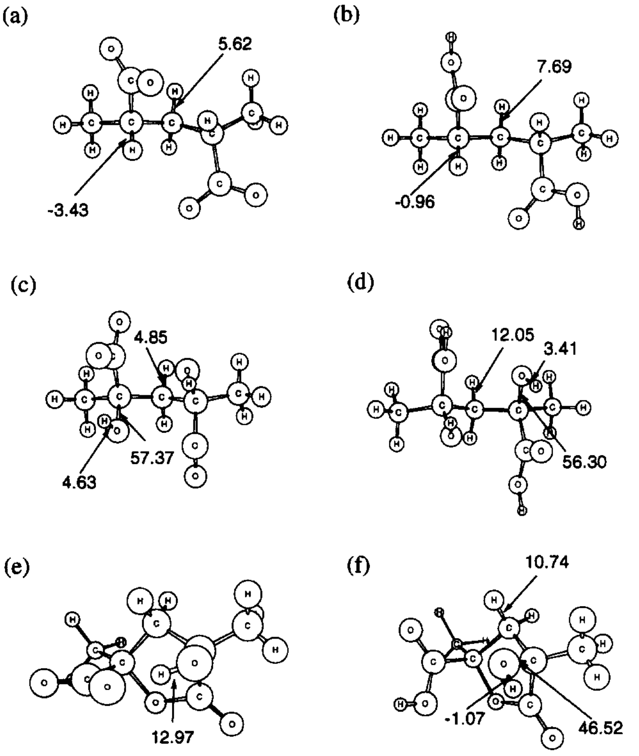

Figure 1 Heats (kcal mol^{-1}) of H and OH abstraction reactions by OH radical. (a) Dissociated form of PAA; (b) acid form of PAA; (c) dissociated form of PHA; (d) acid form of PHA; (e) dissociated form of lactone ring; (f) acid form of lactone ring (negative value means exothermic reaction)

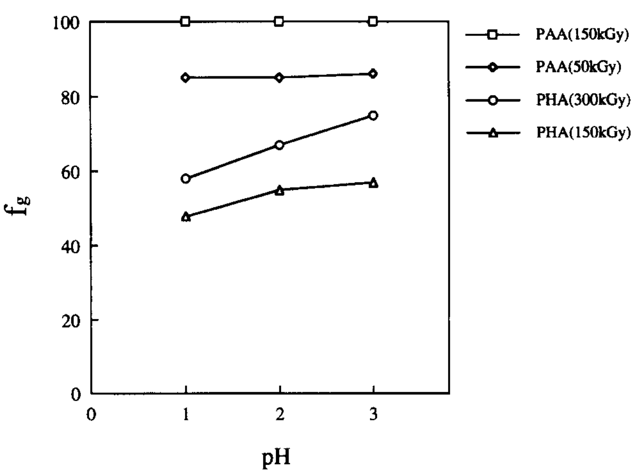

Figure 2 Fraction of gelation of PHA and PAA samples prepared from various pH values

amount of cross-linking sites available on the two polymers. According to our estimation of the dissociated state of the PHA carboxyl group[8], OH groups on a lactone ring which has an undissociated carboxyl group are only 0.17–0.35 per monomer unit at pH 1–3.

The third effect is the most complex; f_g of PHA decreases with decreasing solution pH, whereas f_g of PAA is constant. Here we consider three factors that should influence the cross-linking reaction: (1) the amount of hydroxyl radicals formed by scission of water; (2) the amount of crosslinking sites, that is, the amount of hydroxyl groups and α-hydrogen for PHA and PAA respectively; and (3) the effect of the electrostatic repulsion of the polymer chains.

The first factor, the amount of OH radicals from water, increases with decreasing solution pH[11], irrespective of polymer species, while the other factors depend on the system. For PAA, the amount of potential cross-linking sites is constant. Furthermore, the third factor is almost invariable, since the carboxyl groups on PAA begin to dissociate in the vicinity of pH 3 (in fact, only a few per cent at most dissociate at pH 3). Thus the pH-independence of f_g for PAA seems to be explained in terms of the three factors. On the other hand, the second and third factors in the case of PHA should operate to favour the cross-linking reaction with decreasing pH (the degree of dissociation of PHA has been estimated as ~0–25% for pH 1–3[8]). Thus the experimental result cannot be interpreted in terms of the three factors alone. Although the detailed mechanism is not clear at present, we suppose that an increase in stiffness of the PHA main chain on formation of the lactone ring may prevent the reaction between cross-linking sites.

Swelling behaviour and lactone ring opening

Figure 3 shows swelling ratio (SR) in distilled water for gels which were pretreated by immersion in solutions of various pH. It should be noted that the pH values on the abscissa are those of the external solution before immersion in distilled water, and they also differ from the initial values because of neutralization of charged groups in the gel. For PHA gel, SR increases steeply above pH 6 after a gradual increase up to pH ~5, while for PAA gel, SR starts to increase above pH 5. To examine the correlation of swelling behaviour and lactone ring formation for PHA gel, we attempted to estimate the lactone ring fraction by i.r. measurement. Infrared spectra of these gels are shown in *Figure 4*. Peaks observed at 1775 ± 8, 1724 and 1611 cm^{-1} are assigned to stretching vibration of C=O (lactone ring), stretching vibration of C=O(COOH) and asymmetric stretching vibration of COO$^-$ respectively, as reported in the previous study for the solution system[8]. However, in the present case it is difficult to perform quantitative analysis on the basis of the peak height because baselines cannot be reasonably determined. Hence we attempted a rough

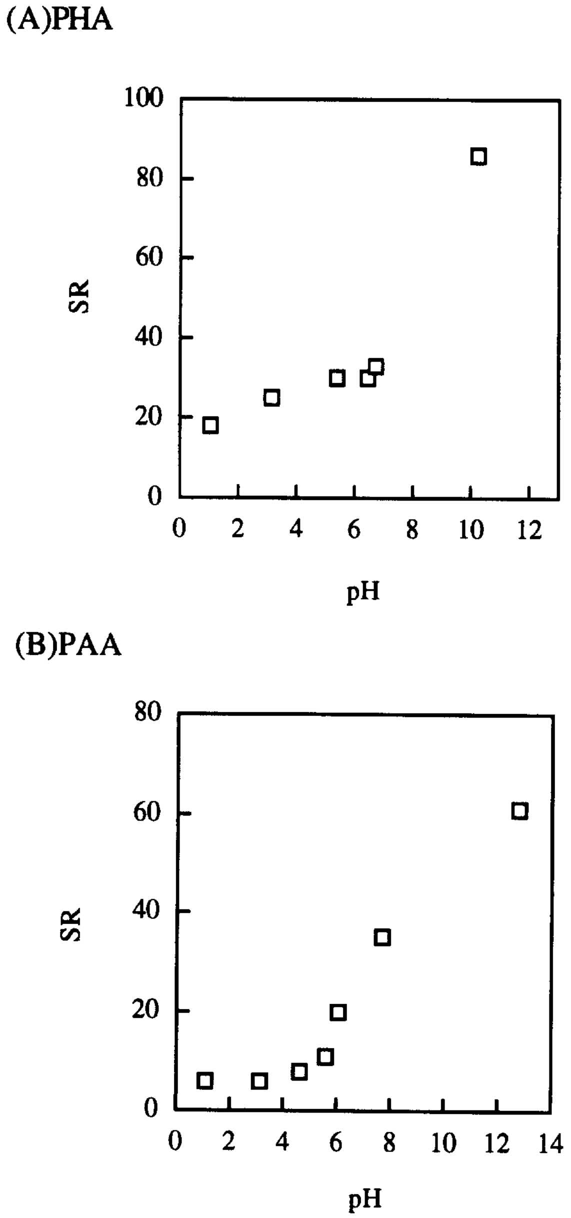

Figure 3 Swelling ratio (SR) of gels in water as a function of pH of pretreatment solutions: (A) PHA; (B) PAA

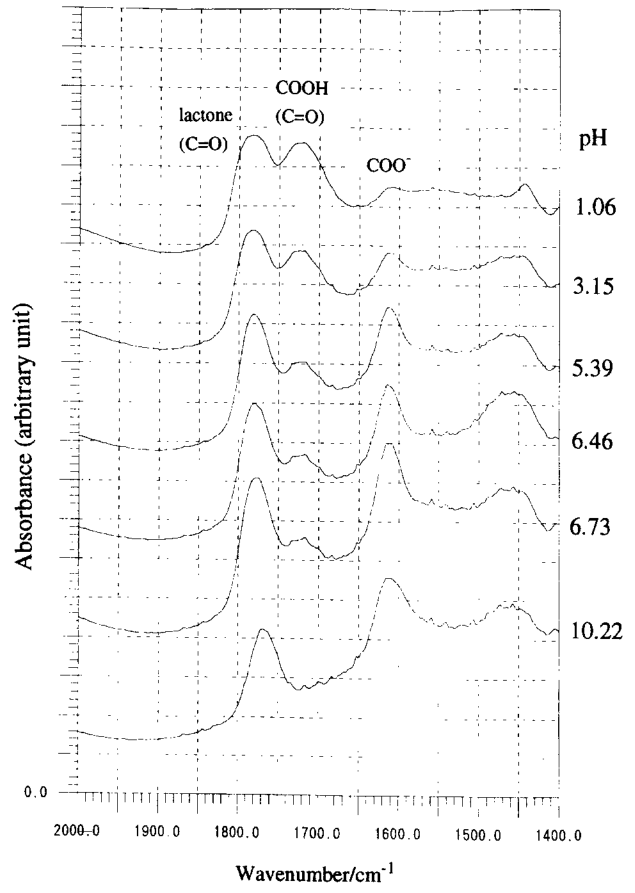

Figure 4 Infrared spectra of PHA gels at various pH values

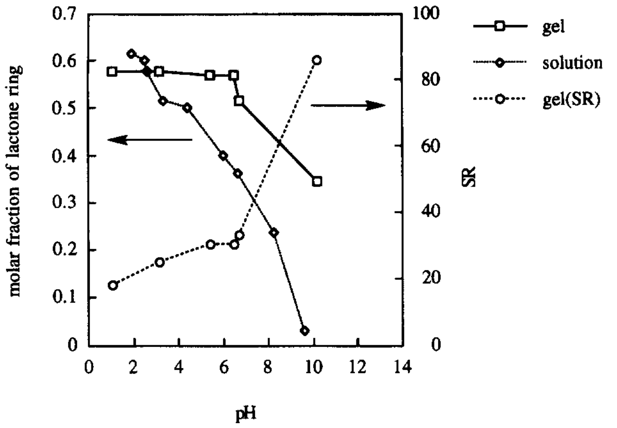

Figure 5 Molar fraction of lactone ring for PHA gels and solutions, estimated by i.r. peak displacement and peak height respectively

estimation of the lactone ring fraction in PHA gel by utilizing the peak displacement of C=O (lactone ring) as a measure of lactone formation. As reported in the previous i.r. study for the solution system, the peak wavenumber shows a characteristic shift with lactone ring formation. The fractions of lactone rings in gel and solution thus obtained are shown in *Figure 5*. It can be seen that the opening of the lactone ring does not proceed in the lower charge density region, or below pH 6. This insensitivity of lactone ring opening to pH change suggests that cross-linkage in the gel significantly retards the ring-opening reaction. The peak shift to lower wavenumber by 15 cm^{-1} which was observed at pH 6.46–10.22 means that the opening of lactone rings occurs only in the alkaline pH region. Therefore, the steep increase in SR above pH 6 may be attributed to the increase in the charge density accompanied by lactone ring opening.

In conclusion, it has been found that gelation of PHA and PAA by γ-irradiation occurs only under acidic conditions. We have proposed a gelation mechanism for PHA, which has no α-hydrogen, on the basis of *ab initio* calculations. Furthermore, it has been shown that the swelling behaviour of PHA gel is strongly dependent on the opening of lactone rings which occurs above pH 6. This last observation suggests that lactone ring formation plays an essential role in the response of PHA gel to external stimuli, such as changes in temperature, solvent and ion binding. Investigation of each of these is now being undertaken.

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