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The Electron Spin Resonance of γ-Irradiated Sodium Polyphosphate. II. Effects of the Degree of Polymerization and the Kind of Cation

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Sodium polyphosphate irradiated with γ-rays was investigated with ESR by varying the degree of polymerization and by replacing sodium ion with other cation. By irradiating at room and liquid nitrogen temperatures and observing ESR at various temperatures, nine kinds of paramagnetic centers were detected. Two of them were attributed to trapped electrons and the others to trapped holes. Four among the latter groups were assigned to radicals on polyphosphate; fragments by bond rupture, $-O_3PO^{\cdot}_{\circ}$ and ${}^{\cdot}_{\circ}PO_3-$, radical on end group, $-O_3PO^{\circ}_{\cdot}$, and radical on chain, $-O_2\dot{P}\overset{\circ}{\ddot{O}}O-$.

The effect of γ-rays on sodium polyphosphate has been investigated as regards its state, glass or crystal, in a preceding paper.1) By the observation of ESR spectra, the color center produced in irradiated polyphosphate has been attributed to the hole trapped on an oxygen atom of PO_4 unit resulting from the rupture of the main chain by γ-irradiation. On the irradiation at room temperature, the ESR spectra have been found in both cases of glass and single crystal doped with a small amount of sulfate, but they have not been detected in the case of the pure single crystal. On the other hand, polyphosphate glass can be treated as a solid polymer composed of linear polychains having a small number of branching points. Accordingly, it is of great interest to inquire the effect of the degree of polymerization on the ESR behavior of the glass. Furthermore, sodium polyphosphate consists of the polyanion of polyphosphate and sodium ion. The study of γ-irradiated sodium polyphosphate can be approached not only from the side of the polyanion by varying the dgree of polymerization, but also from the side of cation by replacing sodium ion with other cations. In this paper, therefore, the irradiated sodium polyphosphate is studied from viewpoints of the effects of the degree of polymerization and kind of cation.

Many glasses including polyphosphate glass have been studied on the effect of the irradiation with γ-rays mostly at room temperature.2-4) As valuable informations were expected to be obtained by the irradiation at low temperature, polyphosphate glass was irradiated not only at room temperature but also at the temperature of liquid nitrogen.

Experimental

Sodium dihydrogen phosphate dihydrate ($NaH_2PO_4\cdot 2H_2O$) and disodium hydrogen phosphate dodecahydrate ($Na_2HPO_4\cdot 12H_2O$) were mixed with each other in a proper mixing ratio and heated at 800°C for 6 hr.5) Sodium polyphosphate glass was obtained by quenching the melt with ice water. The degree of polymerization, which was controlled by the mixing ratio, was determined by the end group titration method 12 hr after the preparation of its aqueous solution.6) By means of this method, we can determine the degree of polymerization of glass whose branching points have been hydrolyzed. In addition to the glasses of various

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1) M. Miura, A. Hasegawa and T. Fukui, This Bulletin, **39**, 1432 (1966).

2) S. Lee and P. J. Bray, *J. Chem. Phys.*, **39**, 2867 (1963).

3) G. O. Krapetyan and D. M. Yudin, *Fiz. Tverd. Tela*, **3**, 2827 (1961).

4) Y. Nakai, This Bulletin, **38**, 1308 (1965).

5) M. Miura, S. Otani, Y. Abe and C. Fukumura, *ibid.*, **36**, 1091 (1963).

6) J. R. van Wazer, *J. Am. Chem. Soc.*, **72**, 647 (1950).

degrees of polymerization, the glasses of lithium, potassium, rubidium, cesium, magnesium, calcium and barium salts were also prepared. These samples were exposed to γ-rays of 5×10^6 R from a ^{60}Co source at the temperature of room or liquid nitrogen.

ESR spectra were obtained by using a Japan Electron Optics Laboratory JES-3BS-X type ESR spectrometer at microwave frequency of 9400 Mc/sec operating with a 100 kc/sec field modulation. Part of measurements were carried out by a Japan Electron Optics Laboratory JES-3BX type ESR spectrometer, in Okayama University, at microwave frequency of 2300 Mc/sec operating with a 100 kc/sec field modulation.

Results and Discussion

Irradiation at Room Temperature. Several glasses having different degrees of polymerization were irradiated at room temperature. Each of their ESR spectra, as shown in Fig. 1, has two weak asymmetric spectral lines at the positions considerably far from the center. The relative intensity of these two lines to the lines near the center decreases rapidly with the increase in the degree of polymerization of irradiated glass. This is due to the fact that the G-value of γ-bombardment to produce the paramagnetic centers responsible for the latter lines increases with the increase in the degree of polymerization, as will be described later.

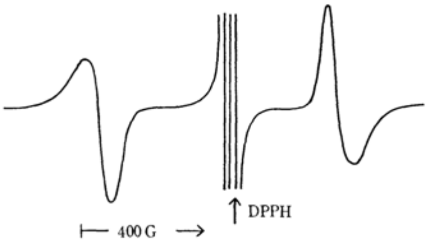

Fig. 1. ESR spectrum of sodium polyphosphate ($\bar{n}=10$) γ-irradiated at room temperature.

For the glass having high degree of polymerization, therefore, these two lines disappeared as had been reported by Nakai,$^{4)}$ but we could find them by the observation with high signal gain. Experiments of the thermal bleaching and power saturation showed that they behave in the same way with each other. These observations suggest that they are the components of a doublet. However, Nakai has ascribed them to the trapped hole and trapped electron. In order to inquire this point in more detail, the measurement of ESR was carried out with K-band: the spacing between these two lines and their widths showed no change compared with those obtained with X-band. This means that they are attributed to a doublet. Nakai has recently agreed to this result by his private communication.

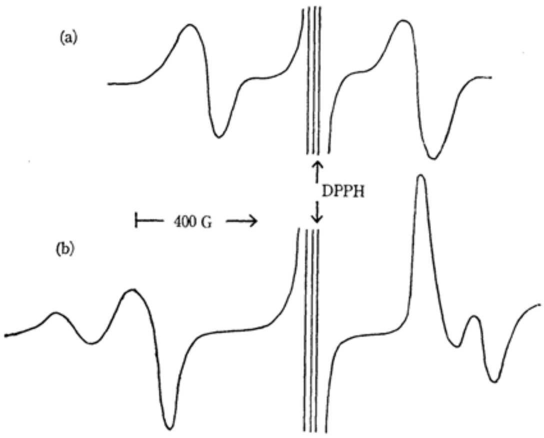

Fig. 2. The variation of the ESR spectrum with the alternation of cation.
(a) Cs, (b) Mg

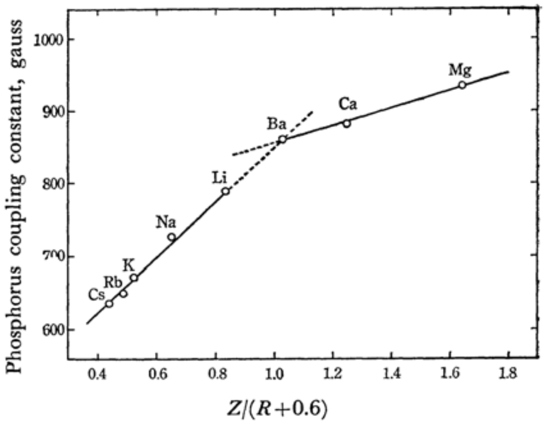

Fig. 3. Correlation between the coupling constant on phosphorus and the value of $Z/(R+0.6)$.

Since among the components of the glass only phosphorus atom has a nuclear spin 1/2, this doublet must originate in the paramagnetic center on phosphorus atom. The g value of the doublet is 2.015 which is larger than that of free spin, 2.0023. This shows that the center is due to the hole trapped by phosphorus atom. The coupling constant of the doublet depends not upon the degree of polymerization but upon the kind of cation.

It is of great interest that the linear relations as shown in Fig. 3 exist between the coupling constant of this radical and the value of $Z/(R+0.6)$, where Z is a charge number of cation and R Pauling's cationic radius in Å.$^{7)}$ The same relation has been found for the coupling constant of nitrogen in the ion pair complexes of m-iodonitrobenzene with alkali and alkaline earth metals.$^{8)}$ The

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7) L. Pauling, "Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca (1960), p. 514.

8) K. Nakamura, This Bulletin, **40**, 1 (1967).

coupling constant increases with the decrease in the radius of cation and with the increase in its charge; it depends upon the field strength of cation. This field induces the phosphorus atom to polarize positively. The positive charge thus produced on phosphorus atom causes the spin density of the hole on it to increase. Accordingly, as phosphorus atom is polarized, the spin density on phosphorus atom increases.

The shape of the spectral line changes with the field strength. It is almost symmetrical for rubidium and cesium salts, but it becomes asymmetrical with the increase in the field strength and finally has an appearance of being splitted into two lines, *e. g.* in the case of magnesium salt. The asymmetry of hyperfine indicates the mixing of the large anisotropies of coupling constant and g value. The qualitative explanation for the line shape on magnesium salt was attempted in terms of anisotropies of coupling constant⁹⁾ and g value in Fig. 4.¹⁰⁾

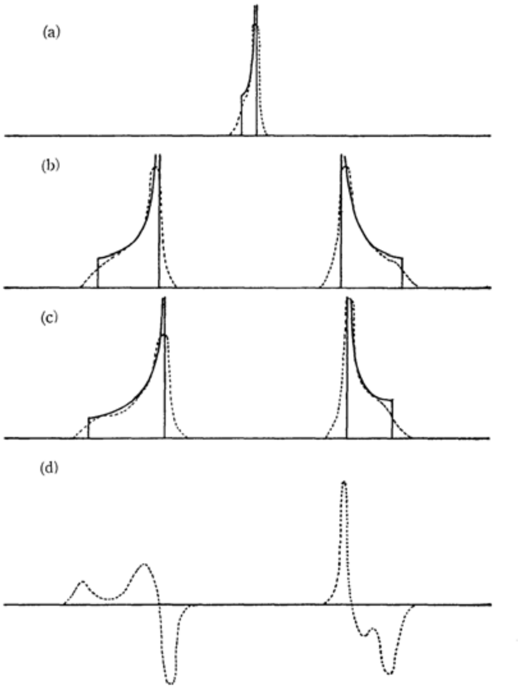
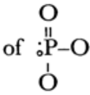
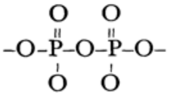
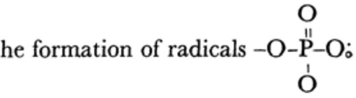
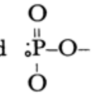
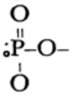
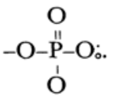
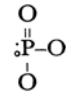
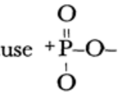
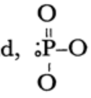


Fig. 4. Qualitative explanation for the shape of the spectral lines in terms of (a) anisotropy of g value, (b) anisotropy of coupling constant, (c) resultant and (d) the first derivative. The dotted lines include a distribution function.

A phosphorus atom combines with oxygen atoms by four σ-bonds of sp^3 hybridization and one π-bond of 3d orbital. The coupling constants for 3s and 3p orbitals of ^{31}P have been theoretically calculated to be 3630 and 205 gauss respectively.¹¹⁾ If this hole occupies the σ-bond, *e. g.* in sodium salt, about 60% of spin density is expected to exist on 3p orbitals as 20% of the spin density does on 3s orbital; this gives about 120 gauss as the value of the anisotropic coupling constant which sufficiently accounts for the asymmetry of spectral lines. On the other hand, if the hole is trapped on the π-bond, the spin densities on 3s and 3p orbitals may be induced by the σ-π interaction or the exchange interaction. But the coupling constant expected from the σ-π interaction may be smaller than those observed here, because the greater part of the spin density is expected on 3s and 3p orbitals, *e. g.* for magnesium salt.

The doublet, therefore, may be originated from σ-radical of  $:\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{P}}}\mathrm{-O-}$. The anisotropies described above correlate with the deformation of the radical by the coordinate formation of cation. From the facts that the doublet is not affected by the degree of polymerization and can not be found on irradiated sodium orthophosphate, the following scheme may be given to the doublet: the bond of  $\mathrm{-O-}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{P}}}\mathrm{-O-}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{P}}}\mathrm{-O-}$ in main chain is ruptured by γ-rays resulting in the formation of radicals  $\mathrm{-O-}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{P}}}\mathrm{-O}:$ and  $:\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{P}}}\mathrm{-O-}$ described as I and II in Table 1 respectively. The intensity of the doublet due to  $:\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{P}}}\mathrm{-O-}$ radical is very weak compared to that due to  $\mathrm{-O-}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{P}}}\mathrm{-O}:$. This may be attributable to the low G value for the production of  $:\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{P}}}\mathrm{-O-}$ radical because  $^{+}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{P}}}\mathrm{-O-}$ ion is also formed by γ-irradiation.

On the other hand,  $:\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{P}}}\mathrm{-O}$ radicals have been reported on the irradiation of $Na_2HPO_3 \cdot 5H_2O$,¹²⁾

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9) E. L. Cochran, F. J. Adrian and V. A. Bowers, *J. Chem. Phys.*, **34**, 1161 (1961).
10) F. K. Kneubühl, *ibid.*, **33**, 1074 (1960).
11) M. C. R. Symons, *Advan. Phys. Org. Chem.*, **1**, 332 (1963).
12) A. Horshield, J. R. Morton and D. H. Whiffen, *Mol. Phys.*, **4**, 475 (1961).

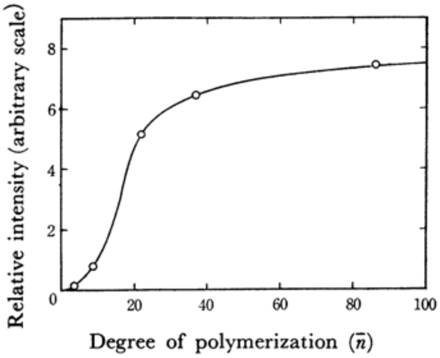

Fig. 5. Relative intensity of ESR spectrum and degree of polymerization. Irradiation and measurement were carried out at room temperature.

$MgHPO_3 \cdot 6H_2O$,[13] $(NH_4)_2H_2P_2O_6$,[14] $(NH_4)_2 \cdot HPO_4$[15] and $(NH_4)_2PO_3F \cdot H_2O$,[16] but they are not same as the radical desribed here, because the latter is a polymer radical.

There is another doublet with the maximum intensity in the vicinity of center of the ESR spectrum in Fig. 1. Its intensity is remarkably influenced by the degree of polymerization; the G value of γ-bombardment to produce this doublet decreases with the decrease in the degree of polymerization (Fig. 5). The changes of the splitting and the line width of the doublet seem to have correlation with each other (Fig. 6). The doublet found on the glass with high degree of polymerization is perfectly coinsident with that reported in the preceding paper.[1] However, the detailed interpretation for this doublet must be postponed until the experiments described in the later part of this paper.

Other weak spectral lines arise distinctly as the degree of polymerization decreases (Fig. 6). These spectral lines showed great resistance to thermal bleaching. After the paramagnetic center described above had bleached out at 200°C, the ESR spectrum still remained was found to consist of three sharp lines and an asymmetric broad line due to anisotropy of g value (Fig. 7). The g values for the sharp lines are 2.011, 2.005 and 2.002 and that for broad line is 2.014 which is the mean value of two of 2.004 and one of 2.035. Their behaviors to the thermal bleaching and the power saturation are almost similar to one another. These spectral lines do not bleach out till the glass is heated to be opaque. Every sodium glass with different degree of polymerization gives these centers, whereas trisodium orthophosphate gives no such centers. They were also found in Li, Na, and K salts, though their difference due to the kinds of the cations was not so evident. The centers for these spectral lines, therefore, can not be discussed in detail, but observations described above presumably allow the speculation that the centers with g values more than 2.0023 are due to the hole trapped by network of glass (V, VI and VII in Table 1) and the other is due to the electron trapped by network of glass (VIII).

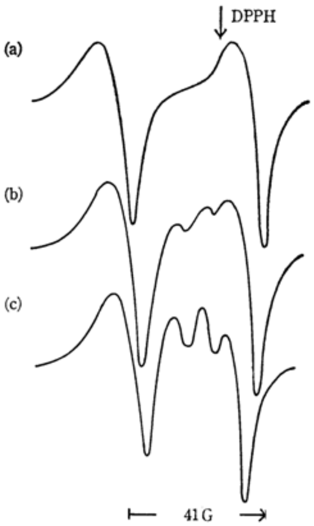

Fig. 6. ESR spectra of sodium polyphosphates irradiated at room temperature and measured at liquid nitrogen temperature.
(a) $\bar{n}=86$, (b) $\bar{n}=11$, (c) $\bar{n}=4.8$.

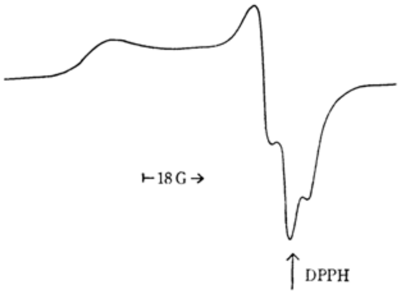

Fig. 7. ESR spectrum of irradiated sodium polyphosphate ($\bar{n}=86$) after heated to 200°C for 15 min.

Irradiation at the Temperature of Liquid Nitrogen. Many kinds of polyphosphate glasses were irradiated at the temperature of liquid nitrogen (−196°C). ESR measurements were carried out at various temperatures.

According to the observation at −196°C, each of the glasses exhibited two lines. The line widths and the separation for the glasses having higher degree of polymerization are larger than those for the glasses of lower degree of polymerization. By

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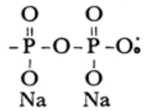
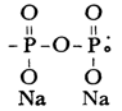
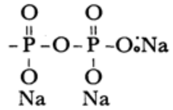
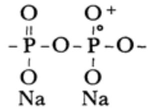
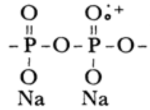
[13] M. W. Hanna and L. J. Altman, *J. Chem. Phys.*, **36**, 1788 (1962).
[14] J. R. Morton, *Mol. Phys.*, **6**, 193 (1963).
[15] J. R. Morton, *J. Phys. Chem. Solids*, **24**, 209 (1963).
[16] F. G. Herring, J. H. Hwang, W. C. Lin and C. A. McDowell, *J. Phys. Chem.*, **70**, 2487 (1966).

Table 1. Paramagnetic centers obtained by γ-irradiation of sodium polyphosphate

Paramagnetic center		Coupling const. (gauss)	g Value	Stability	Intensity
I	 $-\overset{O}{\overset{\Vert}{\underset{\underset{Na}{O}}{\underset{\vert}{P}}}}-O-\overset{O}{\overset{\Vert}{\underset{\underset{Na}{O}}{\underset{\vert}{P}}}}-O^{\cdot}_{\circ}$	40.9	2.009	Stable	Strongest
II	 $-\overset{O}{\overset{\Vert}{\underset{\underset{Na}{O}}{\underset{\vert}{P}}}}-O-\overset{O}{\overset{\Vert}{\underset{\underset{Na}{O}}{\underset{\vert}{P^{\cdot}_{\circ}}}}}$	725	2.015	Stable	Strong
III	 $-\overset{O}{\overset{\Vert}{\underset{\underset{Na}{O}}{\underset{\vert}{P}}}}-O-\overset{O}{\overset{\Vert}{\underset{\underset{Na}{O}}{\underset{\vert}{P}}}}-O^{\cdot}_{\circ}Na$	32	2.008	Stable	Weak
IV	 $-\overset{O}{\overset{\Vert}{\underset{\underset{Na}{O}}{\underset{\vert}{P}}}}-O-\overset{O^{+}}{\overset{\vert^{\circ}}{\underset{\underset{Na}{O}}{\underset{\vert}{P}}}}-O-$ or  $-\overset{O}{\overset{\Vert}{\underset{\underset{Na}{O}}{\underset{\vert}{P}}}}-O-\overset{O^{\cdot +}_{\circ}}{\overset{\Vert}{\underset{\underset{Na}{O}}{\underset{\vert}{P}}}}-O-$	45	2.010	Unstable	Weak
V	Trapped hole		2.014	Very stable	Weak
VI	Trapped hole		2.011	Very stable	Weak
VII	Trapped hole		2.005	Very stable	Weak
VIII	Trapped electron		2.002	Very stable	Weak
IX	Trapped electron		1.995	Unstable	Weak

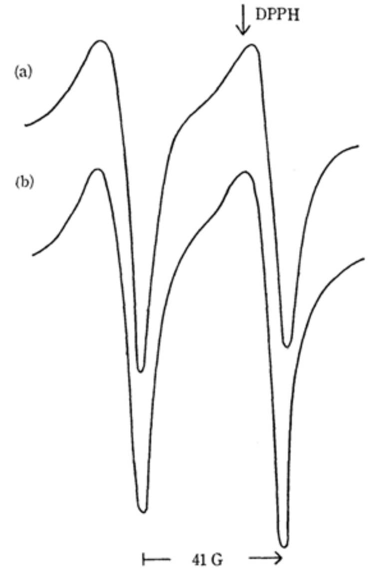
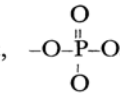


Fig. 8. ESR spectra of sodium polyphosphate glass ($\bar{n}=86$) irradiated and measured (a) at liquid nitrogen temperature and (b) at room temperature.

means of the second derivative, however, two lines for the former glasses are separated to five lines. Two of them are a doublet quite same as that found on the glasses having lower degree of polymerization, one is a singlet at $g=1.995$ and the other two, which are weak, may be a doublet. Latter three spectral lines disappeares as the temperature was elevated up to about -110°C and were slightly affected by the kind of cation. Speculating from their g values, the singlet is due to trapped electron and the weak doublet is due to the hole which is possibly trapped by the non-bonding orbital or π-bond orbital of the oxygen excluded from the main chain of polyphosphate.

On the other hand, the doublet having strong intensity, regardless of the degree of polymerization and kind of cation, gives the same ESR spectrum as that has been reported on irradiation of the glass with high degree of polymerization.[1] This doublet has been attributed to the hole trapped on oxygen atom of fragment,  $-O-\overset{O}{\overset{\Vert}{\underset{\underset{}{O}}{\underset{\vert}{P}}}}-O^{\cdot}_{\circ}$, resulting from the rupture of P–O–P bond. As the temperature was raised up to 100°C, this doublet bleached out. The higher the degree of polymerization of irradiated glass is, the more rapidly the doublet bleaches. The bleaching velocity closely correlates with the easiness of the thermal motion of segments in the glass. The details of this problem will be discussed in another paper, in relation of the bleaching velocity to the crystal fields in polyphosphate glasses.

ESR measurements at various temperatures offered the following facts. As the temperature rises, the spacing of the two lines which appear on the irradiated glasses with low degree of polymerization seems to become smaller. But no glass with high degree of polymerization shows such a behavior. This means that the two lines

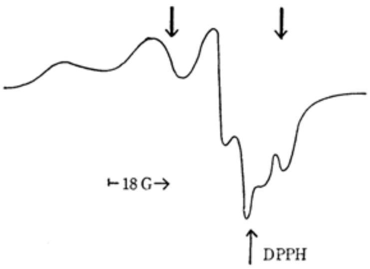


Fig. 9. ESR spectrum of irradiated sodium polyphosphate ($\bar{n}=4.9$) after heated at 100°C for 15 min. Broad arrows show an additional doublet.

for the glass with low degree of polymerization are composed of two doublets. One is quite same as the radical I in Table 1 and the other has a smaller coupling constant. The resistance to thermal bleaching for the former depends greatly upon the degree of polymerization and it is stronger for the latter than for the former (Fig. 9). Thus both of the content of the end groups and the result of thermal bleaching lead the ratio of the latter doublet to the former one to increase. The latter doublet, therefore, must originate from end groups and its coupling constant and *g* value are 32 gauss and 2.008 respectively. Considering from the *g* value, this doublet may be caused by the hole, which is shared to phosphorus, trapped by one of oxygen atoms of one end group. This model is supported by the fact that the line width in Cs glass or Rb glass with low degree of polymerization is broadened presumably due to the very low spin density on these cations.

Conclusions

By changing the conditions of measurement and irradiation, varying the degree of polymerization and replacing sodium ion with other cations, nine paramagnetic centers were separated from the ESR spectrum of γ-irradiated sodium polyphosphate, as are shown in Table 1.

The authors wish to express their hearty thanks to Professor Satoru Tsuda, Mr. Akira Yokohata and Mr. Osamu Yamamoto of Hiroshima University for kindly offering facilities for the γ-irradiation and to Professor Sumitada Asano of Okayama University for making the ESR spectrometer with K-band available for their present work.