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The Electron Spin Resonance of γ-Irradiated Sodium Polyphosphate. I. The Glass and the Single Crystal

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Under irradiation with γ-rays at room temperature, the glass of sodium polyphosphate or its single crystal doped with sodium sulfate becomes red, whereas the pure single crystal remains colorless. The glass and the doped single crystal exhibit ESR spectra which can be attributed to the hole trapped in the non-bonding orbital on the oxygen atom. The pure single crystal, of course, exhibits no ESR spectra. The determination of the degree of polymerization in the aqueous solution of the glass showed a decrease in the length of the main chain caused by the γ-ray irradiation. It may be concluded from these facts that the P–O–P bond is ruptured under the irradiation and that the effect of γ-rays on sodium polyphosphate is closely correlated with the local strain of the P–O–P bond.

A number of works have shown that a glass develops a color under exposure to ionizing radiation. The electron spin resonance (ESR), which has been remarkably developed, has become a most important means for the study of the coloration induced by such irradiation. ESR studies have already been made of irradiated silicate,[1] borate,[2] and phosphate glasses.[3] As to the γ-irradiated phosphate glass, Krapetyan and Yudin,[3a] observing the ESR spectrum consisting of a two-line hyperfine structure, have concluded that the spectrum is caused by an electron trapped on the phosphorus atom. By taking g values and coupling constants into account, however, it has recently been pointed out that the spectrum is to be attributed to the hole trapped by the oxygen atom rather than to the electron trapped by the phosphorus atom.[3b,c]

In ESR investigations, powder and glassy samples have hitherto been used. It is, however, more valuable to deal with a single crystal, since the data from the single crystal give directly not only three g values and coupling constants, but also the orientation of the radical. Therefore, the present investigation has been undertaken in order to obtain the ESR signals from the γ-irradiated single crystal of sodium polyphosphate, to analyze them, and then to compare them with those from the γ-irradiated glass. A mechanism for the coloration caused by the irradiation will also be discussed in this paper.

Experimental

The melt of sodium polyphosphate $(NaPO_3)_n$ was prepared by heating sodium dihydrogen phosphate dihydrate ($NaH_2PO_4 \cdot 2H_2O$) at 800°C for 6 hr. The glass of sodium polyphosphate was obtained by quenching the melt rapidly on dry ice; the single crystal was grown in the melt by slowly cooling and seeding it.[4] The single crystal of sodium polyphosphate doped with a small amount of sodium sulfate (the atomic ratio of sulfur to phosphorus: 1/100) was prepared by the same procedure as was used in the case of the pure single crystal. By X-ray diffractions, both of these crystals were identified as Type A of Kurrol's sodium salt,[5] which is a monoclinic crystal with the space group of $P2_1/n$ and the following crystallographic constants:

$a=12.12$ Å; $b=6.20$ Å; $c=6.99$ Å; $\beta=92°$.

These crystals have definite faces of cleavage (101) and plane $(\bar{3}01)$.

These samples were exposed to γ-rays of 5×10^6 r. from a ^{60}Co source at room temperature. The ESR measurements were carried out at room temperature.

In an irradiated single crystal doped with sulfate, a rectangular co-ordination system, a'b'c', was selected for convenience; the a' axis is perpendicular to the plane of $(\bar{3}01)$, the b' axis is identical with the crystallographic b axis, and c' axis is perpendicular to a' and b' axes. The crystal was rotated upon each of these axes in turn, and the ESR spectra were recorded at intervals of 15°.

The ESR spectra were obtained by using a T.D.S. (Tokyo Denki Seiki) Model T-5000 ESR spectrometer at a microwave frequency of 9225 Mc./sec. for the X-band and at one of 23000 Mc./sec. for the K-band

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1) S. Lee and P. J. Bray, *Phys. Chem. Glass*, **3**, 37 (1962); C. M. Nelson and R. A. Weeks, *J. Am. Ceram. Soc.*, **43**, 399 (1960).

2) a) S. Lee and P. J. Bray, *J. Chem. Phys.*, **39**, 2863 (1963); b) S. Lee and P. J. Bray, ibid., **40**, 2982 (1964).

3) a) G. O. Krapetyan and D. M. Yudin, *Fiz. Tverd. tela*, **3**, 2827 (1961); b) Y. Nakai, This Bulletin, **38**, 1308 (1965); c) T. Feldmann, A. Treinin and V. Volterra, *J. Chem. Phys.*, **42**, 3366 (1965).

4) E. Thilo, G. Schulz and E. M. Wichmann, *Z. anorg. u. allgem. Chem.*, **272**, 182 (1953).

5) K. H. Jost, *Acta Cryst.*, **14**, 844 (1961).

operating with a 100 kc./sec. field modulation. The g values were determined by comparing them with the value for DPPH, by using DPPH and a gaussmeter by means of nuclear magnetic resonance.

The viscosities of aqueous solutions of non-irradiated and γ-irradiated (7.8×10^7 r.) glasses were measured[6] at the concentration of 0.80 g./100 ml. and at 25°C (Fig. 2). The degrees of the polymerization of non-irradiated and irradiated glasses were determined by the pH titration of end groups[7] after the hydrolysis at the branching points had been completed (Fig. 3).

Results and Discussion

Sodium Polyphosphate Glass.—When sodium polyphosphate glass was irradiated with γ-rays, it turned dark red and exhibited two asymmetric ESR absorption lines (Fig. 1). The width of these

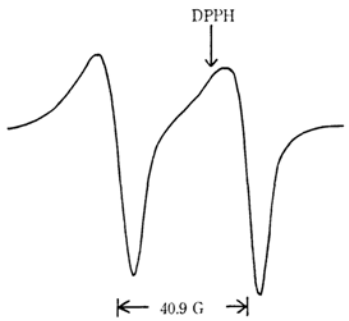


Fig. 1. The ESR spectrum of the γ-irradiated sodium polyphosphate glass at room temperature.

absorption lines at the temperature of liquid nitrogen is a little narrower than that at room temperature. These ESR spectra, as reported by some authors,[3] seem to be a doublet arising from the hyperfine structure due to the ^{31}P nucleus. The following facts are also known: they are not affected by the kind of cation and they are closely correlated with the visible absorption band with a maximum absorption at ca. 500 mμ. By taking account of the ESR spectrum consisting of the repetition of an asymmetric absorption line, this doublet is expected to have a practically isotropic coupling constant and three different g values; two of them resemble each other, and the other is the largest.

Sodium polyphosphate glass has branching points which are unstable and are easily hydrolyzed in the aqueous solution. The degradation at branching points can be detected by the decrease in the viscosity of the aqueous solution;[6] it is completed after about 8 hr. at 25°C, as may be seen in Fig. 2. This figure also shows that the γ-irradiation reduces the viscosity of the aqueous

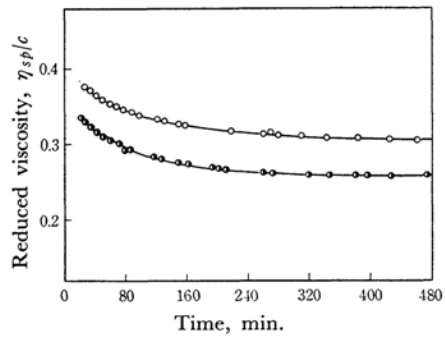


Fig. 2. Time dependence of the viscosity of the aqueous solutions of non-irradiated (○) and γ-irradiated (◑) glasses. $c=0.80$ g./100 ml. 25°C

solution of the glass without having an appreciable effect on the degradation at branching points. Further, the degree of polymerization, $\bar{n}$, decrease with the increase in irradiation dose, as is shown in Fig. 3, where $\bar{n}$ of non-irradiated glass is also

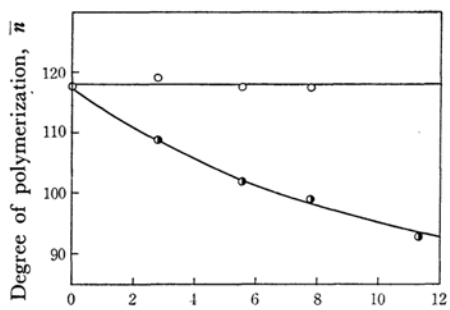


Fig. 3. The decrease in the degree of polymerization of polyphosphate glass with the irradiation dose.
○ stored in the room
◑ irradiated with γ-rays at 1×10^5 r/hr.

plotted against its storage period. These results show that the main chain of polyphosphate is ruptured by γ-irradiation.

The Pure Single Crystal of Type A of Kurrol's Sodium Salt.—The single crystsl of Type A of Kurrol's sodium salt irradiated with γ-rays at room temperature gave neither color nor any ESR absorption, even at the temperature of liquid nitrogen. When the single crystal, a part of which was covered with the glass, was irradiated, the glassy part turned dark red, but the part of the single crystal underneath acquired no color. Irradiation with γ-rays at room temperature seems to have no lasting effect on the pure single crystal of Kurrol's sodium salt.

The Single Crystal of Type A of Kurrol's Sodium Salt Doped with a Small Amount of Sodium Sulfate.—According to the facts described above, the effect of γ-rays on sodium polyphosphate seems to depend remarkably on its state, whether

6) U. P. Strauss, E. H. Smith and P. L. Wineman, *J. Am. Chem. Soc.*, **75**, 3935 (1953).
7) J. R. van Wazer, ibid., **72**, 647 (1950).

it is glassy or crystalline. In order to investigate the primary factor for this phenomenon and to speculate on the mechanism of the coloration, we attempted to inquire into the single crystal incorporating an impurity. Sodium sulfate was selected as the impurity because its structure is similar to PO_4. The single crystal of Kurrol's sodium salt doped with sodium sulfate was colorless and gave no ESR absorption before exposure to γ-rays, but it turned red and gave five ESR absorption lines after such exposure. Four of these lines show almost the same intensity, while the fifth one, which will be discussed below, shows a very weak intensity. The g values of these ESR absorption lines depend upon the orientation of the single crystal with relation to the direction of the magnetic field. The ESR spectra obtained when c' axis of the single crystal is parallel to the direction of the magnetic field are illustrated in Fig. 4, where

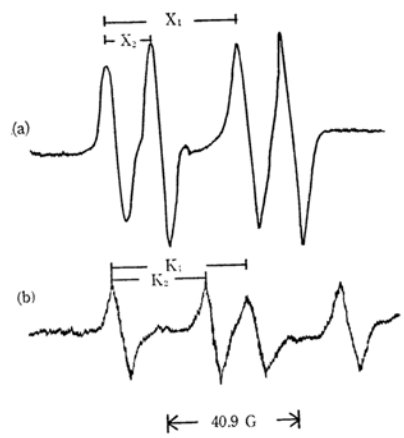


Fig. 4. The ESR spectra for the single crystal doped with sodium sulfate with (a) X-band and (b) K-band.

Fig. 4(a) shows the result with an X-band and Fig. 4(b) that with a K-band. The X_1 spacing shown in Fig. 4(a) is equal to the K_1 spacing in Fig. 4(b), and X_2 is about 1/2.5 times K_2; the frequency of the microwave has an influence not on the spacings X_1 and K_1, but on X_2 and K_2. These four absorption lines, therefore, are due to two doublets originating from two magnetically nonequivalent sites in the single crystal. These doublets are hyperfine structures arising from the interaction between an unpaired electron and a ^{31}P nucleus. The values of their coupling constants are equal to each other and are the same as that from the irradiated glass.

Figure 5 shows the variation in the four ESR absorption lines with the orientation of the single crystal in relation to the magnetic field. From these calculated components, the principal values of g and the direction cosines of the principal axes were evaluated as is shown in Table I. These principal values are different from one another;

TABLE I. PRINCIPAL VALUES AND THEIR DIRECTIONS.

Principal values	Direction cosines in a'b'c' axis system			
$g_1=2.006_4$	−0.496	−0.024	0.868	(I)
	0.995	−0.078	0.045	(II)
$g_2=2.008_2$	−0.123	0.314	0.945	(I)
	0.983	−0.157	0.024	(II)
$g_3=2.016_1$	0.912	0.111	0.395	(I)
	−0.330	0.009	−0.944	(II)

* (I) and (II) arise from two different nonequvalent sites.

g_1 is close to g_2, g_3, is largest, and all of them are larger than the value of the free spin, $g=2.0023$.

The isotropic coupling constant, A_{iso}, was determined from the spacing of the hyperfine structure, while the anisotropic coupling constant, B_{aniso}, was estimated from the anisotropic coupling components (<1 Gauss) in each plane.

$$A_{iso} = 50.9 \text{ Gauss}$$

$$B_{aniso} = 3\text{—}5 \text{ Gauss}$$

Here, this hyperfine structure is due to the interaction of an unpaired electron with a ^{31}P nucleus; the contributions to the hyperfine coupling constant from 3s and 3p electrons of the ^{31}P atom have already been calculated:[8]

$$A_{3s} = 3630 \text{ Gauss}$$

$$B_{3p} = 204.8 \text{ Gauss}$$

From the values of A_{iso}, B_{aniso}, A_{3s} and B_{3p}, the spin densities on the ^{31}P atom were calculated to be as follows:

$$\rho_{3s} = 1.1\%$$

$$\rho_{3p} \simeq 2\%$$

where ρ_{3s} and ρ_{3p} are the spin densities in the 3s and 3p orbitals of the phosphorus atom respectively. The phosphorus atom of polyphosphate, however, seems to combine with the oxygen atom by using its sp^3 hybridization.[9] Accordingly, the estimated spin density for the 3p orbital is smaller than the value expected from the 3s spin density.

The rest of the spin density, ca. 97%, may exist in the non-bonding orbital of the oxygen atom. Since the ESR spectrum of this single crystal, as will be described below, is equivalent to that of the glass which is independent of the kind of cation, the color in this single crystal seems to be due to the hole trapped in the non-bonding orbital of an oxygen atom shared by two phosphorus atoms before irradiation.

These spectra are also equivalent to that observed by Nakai.[3b] He has attributed the spectrum to

8) M. C. R. Symons, *Advances Phys. Org. Chem.*, 1, 332 (1963).
9) J. R. van Wazer, "Phosphorus and its Compounds. I," Interscience Pub. Inc., New York (1958).

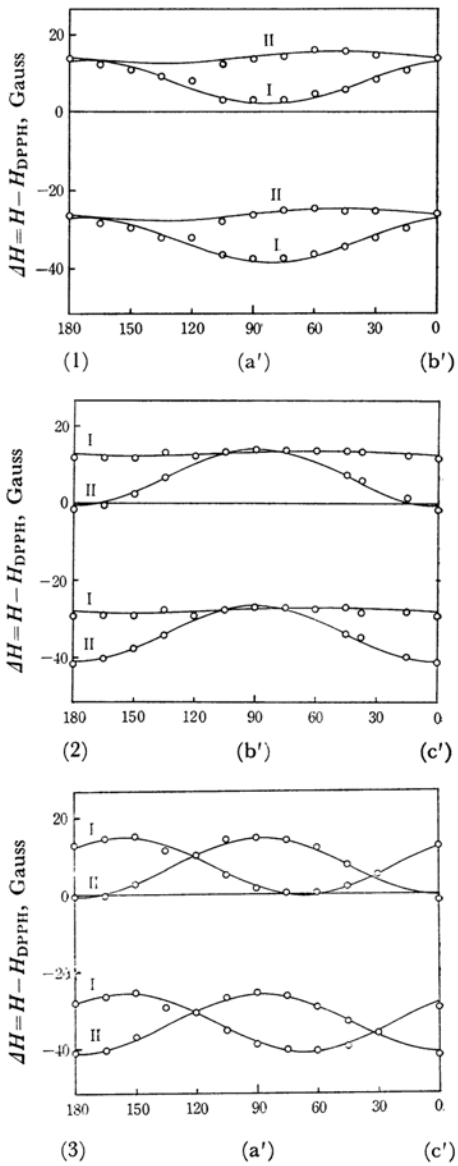


Fig. 5. Observed values and calculated curves for the hyperfine structure in the single crystal doped with sodium sulfate relative to the resonance of DPPH; the magnetic field being parallel to (1) a′b′, (2) b′c′ and (3) c′a′ planes. I and II are resonance lines arising from two nonequivalent sites respectively.

the hole trapped on the oxygen atom of the polyphosphate chain (P–O–P). Lee and Bray,[2a] from their study of the borate glass, have suggested that the hole giving rise to the ESR spectrum is trapped on an oxygen atom shared by two boron atoms, one three-coordinated and the other four-coordinated, and that it diffuses one-sidely to the latter atom. In polyphosphate glass, two phosphorus atoms at the branching point probably have somewhat different electronic configurations; therefore, it may be supposed that the hole is trapped on the oxygen shared by these two phosphorus atoms, as in the case of borate glass. However, as may be seen in Fig. 2, the branching point has an unappreciable effect upon γ-ray irradiation, though the degree of polymerization is reduced. Therefore, such a supposition as that described above seems to be unreasonable for the present case.

The crystal structure of Kurrol's sodium salt,[5] with its principal axes, is shown in Fig. 6. There

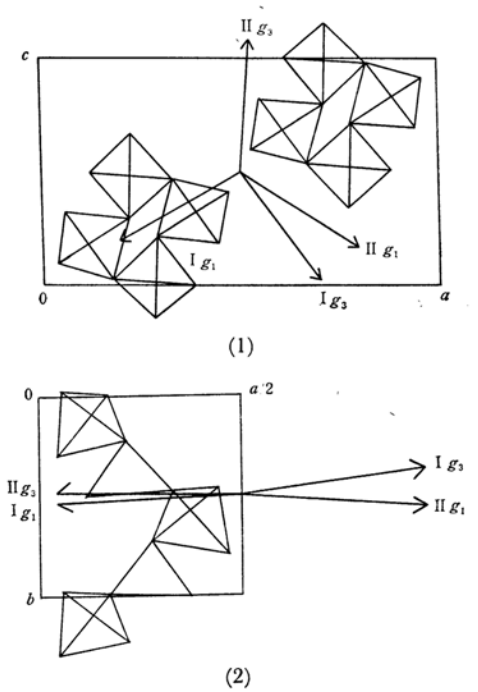


Fig. 6. The orientation of the principal axes against the crystal structure of type A of Kurrol's sodium salt; (1) and (2) are projections to ca and ab planes, where phosphorus atoms exist at the centers and oxygen atoms at the corners of these tetrahedrons.

is a considerable discrepancy between the principal axes and the non-bonding orbitals of oxygen in the main chain to be expected from the crystal structure. The following two explanations for this discrepancy are possible. One is that the center giving rise to the ESR spectrum is near the SO_4^{2-} group, which may exist at the interstice between polyphosphate chains where the chain may experience a local strain. The other is that the P–O–P bond strained by the SO_4^{2-} group is ruptured under the irradiation and that the resultant polyphosphate radicals occupy the stable orientation in the crystal. The latter interpretation is supported by the following facts: the absorption lines of the quartet, which must be expected from two equivalent phosphorus

atoms if the P–Ö–P bond is not ruptured, are not found, and the calculated principal values of g, which are different from one another and are larger than the value of the free spin, suggest that the two bonds in P–Ö–P are not equivalent to each other, but that one of these two bonds is rather ruptured.[10]

The principal values obtained from the irradiated single crystal doped with the sulfate are compared with the ESR spectrum from the irradiated glass in Fig. 7. This comparison obviously shows that

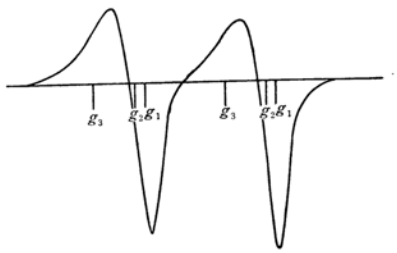
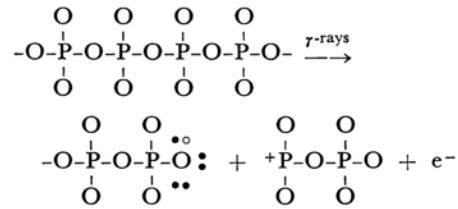


Fig. 7. The comparison between the principal values of g for the doped single crystal and the ESR spectrum of the glass.
$g_1=2.006_4$ $g_2=2.008_2$ $g_3=2.016_1$

the center produced in this single crystal is just the same as that produced in the glass.

On the other hand, the degrees of the polymerization of non-irradiated and irradiated glasses were measured after thermal treatment at 250°C for 6 min. The red color of the irradiated glass was bleached by this treatment. Although the $\bar{n}$ values of both glasses decreased upon this treatment, the value of irradiated glass was distinctly smaller than that of non-irradiated glass (Fig. 8). This indicates that the degree of polymerization, which is reduced by irradiation with γ-rays, is not restored by thermal treatment, though the color is bleached.

In addition to these results, account must be taken of the facts that the ESR absorption lines with a large coupling constant expected from ·P–O–P do not appear, while an additional absorption band, probably due to the scattered electrons, appears in the ultraviolet region. Therefore, the following speculation may be given regarding the mechanism of the coloration by γ-ray irradiation. The P–O–P bond in the glass or the single crystal doped with the sulfate is ruptured under the irradiation, resulting in the production of a radical, a positive ion, and a scattered electron:



The radical thus produced gives rise to the red color.

A weak ESR absorption line in the irradiated single crystal doped with the sulfate was found at $g=2.007$; this absorption line is different from that due to a radical of the sulfate, for the latter was found at $g=2.003$ when the content of the sulfate in the glass increased. The ESR spectrum of irradiated glass has a weak shoulder at $g=2.007$ which becomes more noticeable as the degree of the polymerization of the glass decreases. These observations lead us to the conclusion that the center producing the weak absorption line at $g=2.007$ arises from the hole trapped by oxygen atoms of the end group.[11]

Thus, under irradiation with γ-rays, the single crystal doped with the sulfate acquires the same color center as in the case of the glass, whereas the pure single crystal shows no effect. These phenomena may be interpreted in the following way. The P-O-P bond in the pure single crystal is too stable to be ruptured under the irradiation with γ-rays, whereas the bond near the sulfate in the single crystal is weakened by the local strain caused by the foreign element. The bond in the glass may also be strained, as the glass was prepared by quenching the melt. Such strained bonds are easily ruptured, and the red color results from irradiation with γ-rays.

In conclusion, the effect of γ-rays on sodium polyphosphate seems to be closely correlated with the local strain of the P–O–P bond.

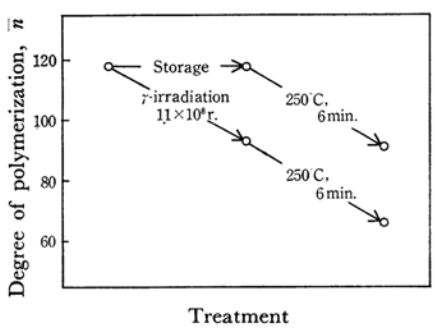


Fig. 8. The variation in the degree of polymerization of the glass with several treatments.

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10) M. C. M. O'Brien, *Proc. Roy. Soc.*, **A231**, 404 (1955).

11) M. Miura and A. Hasegawa, This Bulletin, **39**, 196 (1966).