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IN FOLLOWING PULSE RADIOLYSIS OF
POLYVINYLPIROLIDONE

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ABSTRACT

**LIGHT SCATTERING INTENSITY TECHNIQUE IN FOLLOWING PULSE
RADIOLYSIS OF POLYVINYLPIRROLIDONE.** Light scattering intensity (LSI) study on pulse radiolysis of polyvinylpyrrolidone (PVP) in the presence of oxygen has been done to reconfirm the role of oxygen on the crosslinking and degradation of polyvinylpyrrolidone. Different concentrations of oxygen saturated PVP aqueous solutions were irradiated with electron pulses generated from a LINAC-6 MeV at various dose and then light scattering intensity (LSI) signals were simultaneously observed. It was found that the LSI signals given by the PVP solutions having concentration up to $1.5 \times 10^{-2}M$ decrease for all irradiation doses. However, at higher PVP concentration the LSI signal was found to decrease initially and then increases up to a saturated level. These results indicate that at low concentration of PVP, the oxygen affects the degradation of polymer chain whereas at a higher PVP concentration crosslinking also occurred besides the degradation. It was concluded that the crosslinking of PVP in the presence of oxygen is caused by the reaction of the polymer with peroxide macroradicals formed during irradiation. The possible mechanism of the crosslinking process was proposed.

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ABSTRAK

TEKNIK INTENSITAS HAMBURAN CAHAYA UNTUK MENGIKUTI PROSES RADIOLISIS POLIVINILPIROLIDON. Telah dilakukan studi intensitas hamburan cahaya pada proses radiolisa polivinilpirolidon (PVP) dalam rangka memahami peranan oksigen dalam proses pengikatan silang (crosslinking) dan pelapukan (degradasi) polivinilpirolidon. Berbagai konsentrasi PVP yang dijenuhkan dengan oksigen iradiasi pada berbagai dosis dengan pulsa elektron yang dihasilkan dari mesin pemercepat elektron linear (LINAC-6 MeV). Intensitas hamburan cahaya LSI) yang didapat selama iradiasi pulsa elektron tersebut diamati secara seksama. Didapatkan bahwa larutan PVP yang mempunyai konsentrasi sampai $1,5 \times 10^{-2}M$ semuanya memberi sinyal LSI yang menurun untuk semua dosis iradiasi. Akan tetapi pada konsentrasi PVP yang lebih besar didapatkan sinyal LSI yang mula-mula menaik dan kemudian jenuh. Hal ini menunjukkan bahwa pada konsentrasi yang relatif rendah, oksigen berpengaruh pada pelapukan (degradasi) rantai polimer, sedangkan pada konsentrasi yang relatif lebih tinggi selain degradasi juga terjadi pengikatan silang (crosslinking). Disimpulkan bahwa adanya pengikatan silang PVP yang mengandung oksigen disebabkan oleh reaksi polimer dengan makro radikal peroksida yang terbentuk selama iradiasi.

INTRODUCTION

Light scattering intensity (LSI) is one of the useful methods in studying the pulse radiolysis of polymers (1-3). It has been known that several chemical parameters involve in pulse radiolysis experiment such as the radiation yield of crosslinking and degradation of polymers, the number of

radicals located in individual macromolecules, primary concentration of macroradicals, the kinetic order and the rate constant of reactions could be calculated by using LSI technique⁽²⁾. ROSIAK et.al. ⁽⁴⁾ have reported that oxygen promotes main chain scission of polyvinylpyrrolidone (PVP) represented by decrease of LSI signal. However, the effect of oxygen in various concentrations of PVP solutions during pulse radiolysis has not yet been studied. In order to understand more about the effect of oxygen on the irradiation of PVP, a set of experiment of pulse radiolysis by using LSI technique has been done and the result is reported herewith.

EXPERIMENTALS

Polyvinylpyrrolidone powder K-90 of Fluka AG (Swiss). Its average molecular weight is equal to $M_w = 1.2 \times 10^6$. The solution of polyvinylpyrrolidone in different concentrations were made using bidistilled water, deionized in a device produced by Barnstead Inc. (USA), Nanopure II. Seven kinds of polymer concentrations were prepared : (1.3; 2.1; 2.6; 3.3; 3.8; 5.0; 6.4) $\times 10^{-2}$ b.mole/dm³. Other reagents were analytical grade and used without further purification.

DESCRIPTION OF EQUIPMENT

A linear accelerator ELU-6E of 6 MeV (made in USSR) was used as a source of radiation. The light scattering intensity (LSI) system comprises a unit laser ILA 120 (made in Germany, GDR) and the incident light with wavelength equal to 514 nm and output power of 1.3 W is generated by Ar-He laser source.

Figure 1, shows a layout of the experiment using the LSI system. In the experiment, a photomultiplier EMI 9781 was closely placed to a light guide, gathering the scattered light, transformer the light intensity into electrical signal. An operational amplifier Burr-Brown 3554 transfers this signal to the Faraday cage, in which the rest of detection systems are installed. The signal can be registered by IWATSU 912 digital scope or digitizer DATALAB 912. Next the data are sent to an IBM-XT microcomputer. The time resolution of the full system is 1 μ s as a results of signal-to-noise ratio and the disturbance of undesirable emission from the cell, induced by electron beam.

IRRADIATION OF SAMPLES

The solution of polymers were irradiated with 0.5; 1; 2; 3; and 4 μ s electron pulses of 6 MeV, generated from that electron accelerator ELU-6. Immediately before irradiation, the polymer solutions were bubbled with oxygen for 20

minutes. The intensity of scattered light was then measured under the angle of 90 degrees in relation to the incident light. Dosimetry was performed using Fricke's dosimeter (the solution saturated with oxygen), $G(\text{Fe}^{+3}) = 13.0$.

TREATMENT OF DATA

As shown previously (1), the total extent of LSI decrease R_{∞}^D , observed in the case of main-chain degradation is proportional to Zs , the number of scissions per initial macro molecule :

$$R_{\infty}^D = \frac{U_0 - U_x}{U_x - U_r} = \frac{Zs}{4A_2cP_0M_w(o)+2} \quad (1)$$

where : c -polymer concentration in g cm^{-3} ; $M_w(o)$ - weight average molecular weight; U -signal voltage, proportional to the LSI; the subscripts 0, ∞ and r denote the time before the pulse and the long time after pulse, and solvent, respectively; A_2 -second virial coefficient in $\text{mole cm}^3 \text{ g}^{-2}$; P_0 -particle scattering factor.

Similar relationship hold when LSI increases due to cross-linking :

$$R_{\infty}^C = \frac{U_x - U_0}{U_x - U_r} \quad (2)$$

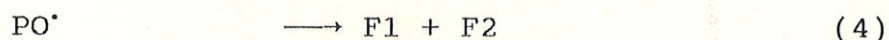
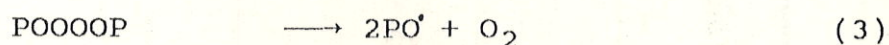
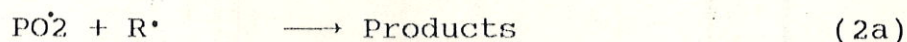
RESULTS AND DISCUSSION

In Fig. 2, are presented typical oscilloscope traces of LSI changes in the aqueous solutions of polyvinylpyrrolidone, saturated with O_2 . Irradiated by electron pulses of aqueous polyvinylpyrrolidone solutions at concentration up to $1.5 \times 10^{-2}M$ causes exclusively the decrease in the LSI signal. After several hundreds of microseconds it attains a new, stable value (see Fig.2,a,b).

A relative degree of degradation R^D increases with the increases of dose per pulse but the half-life time remains stable and amounts to $(\tau_{1/2}) = 0.15 \text{ ms}$ or $150 \mu s$ (see Fig.3,a,b). The decrease in the value of LSI signal is consistent with the kinetics of a first order reaction. Also, changes in the concentration of the solution do not cause any changes in the values of the half-life time (see Fig.3c). The rate constant of the process connected with the decrease of the intensity of scattered light, determined on this basis, is equal to $k_D = 4.7 \times 10^3 \text{ s}^{-1}$. These results are in good agreement with the ones given previously by Rosiak et.al.(4). They have also found, that substances like cysteamine or isopropyl alcohol having an affinity for the radicals when introduced into the polymer solutions bring about decrease in LSI changes but have no effect on the half-life time $\tau_{1/2}$. This is therefore an indication that the time for establishing bond scissions in the main chain is much shorter than $\tau_{1/2}$ of the LSI, and that the latter corresponds to diffusion of

fragments. Their experiments with addition of glycerin confirmed (4), that the LSI changes describe the diffusion of the fragments of broken polyvinylpyrrolidone chain.

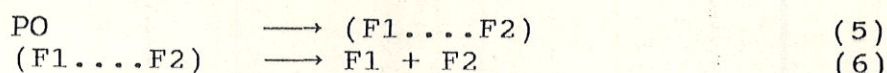
For the explanation of the mechanism of oxygen degradation a following scheme of consecutive reactions is adopted (1) :



In the above scheme, the reaction (2a) denotes non-effective superoxide transformations (in terms of LSI) which do not lead to changes in the molecular weight of the polymer (e.g. formation of hydroperoxides, reactions of disproportionation etc.) (R denotes some transient species of solution's radiolysis).

On the basis of research on the radiolysis of aqueous solutions of polyethylene oxide (PEO) and polyacrylamide (PAA) it has been found that in the suggested scheme of reaction the slowest stage is a bimolecular reaction (3), and its rate determines the rate the whole process. For the above polymer the decrease in the intensity of light scattered by polymer solutions proceeds according to the kinetic equations of a second order one (1, 3, 5).

In the case of the radiolysis of aqueous of polyvinylpyrrolidone this scheme should be supplemented by the reaction of diffusion of broken chain fragments, as the reaction controlling the rate a whole process :



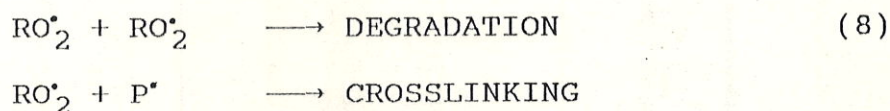
For higher concentrations of polyvinylpyrrolidone, apart from the process of degradation bringing about a decrease in the LSI signal, its increase on the longer time scale is observed for PVP concentrations higher than the critical value ($6.2 \times 10^{-2}\text{M}$) see Fig. 4. The increase in LSI signal indicates that, besides the oxygen degradation, also a crosslinking takes place in the system. This process is similar to the case of argon-saturated PVP solutions, where crosslinking of PVP macroradicals occurs :



The recorded changes are to be explained by considering the competition between the intra and intermolecular process. Intermolecular reactions are prepared in more diluted solution, i.e. in systems characterized by bigger number of radicals localized on one chain. It corresponds to the decrease in the concentration of the solution and at a constant concentration to a higher dose, in such systems the reactions of degradation are dominant.

The optical spectra observed in argon-saturated aqueous PVP solutions have a maximum of absorbance at 390 nm. This absorbance is increased (nearly doubled) in the solutions saturated with N₂O. These results confirm, that polymer macroradicals are formed as a result of hydrogen abstraction by OH radicals from polymer chain. In the presence of oxygen, however, the absorbance spectra does not achieve a maximum as it was obtained in argon saturated polymer solutions. The shape of the spectrum does not change with changes of PVP concentration and of the dose absorbed after electron pulse (see Fig.5). It is an indication, that in the presence of oxygen polymer macroradicals react very fast with oxygen forming peroxy radicals, that do not absorb in the analyzed wavelength range. As the changes in dose and concentration do not change the value of absorbance at 390 nm, it seems that the crosslinking reaction in the presence of oxygen is due to another mechanism than in argon-saturated solutions.

In Fig. 6 the ratio of relative LSI signal $LSI R^D$ to relative in LSI signal due to crosslinking $LSI R^C$ is shown as a function of dose per pulse and the reciprocal of polymer concentration. Considering various decay mechanisms of peroxida radicals that has been found, the experimental data could be explained only by the following scheme :



For the above scheme the velocity of decay of peroxy radicals is described by :

$$-\frac{d[RO_2^{\cdot}]}{dt} = k_1 [RO_2^{\cdot}]^2 + k_2 [P] [RO_2^{\cdot}] \quad (9)$$

where k_1 is the rate constant of degradation and k_2 is the rate constant of crosslinking. The ratio of degradation to crosslinking may be written as :

$$\frac{R_s^D}{R_s^C} = \frac{k_1 [RO_2^{\cdot}]}{k_2 [P]} \quad (10)$$

As (RO_2^{\cdot}) is proportional to the dose, we obtain :

$$\frac{R_s^D}{R_s^C} = K \frac{D}{[P]} \quad (11)$$

According to the above equation, at constant polymer concentration the relationship between degradation/crosslinking ratio and dose should be linear, having the slope of $K/[P]$. At constant dose, the relationship between degradation/crosslinking ratio and the reciprocal of concentration should also give a straight line with the slope equal KD . As can be seen

In Fig. 6a, the relationship $\frac{R_s^D}{R_s^C} = f(D)$ is linear, however

the line does not cross the vertical axis at zero. The

experimental points presented as $\frac{R_s^D}{R_s^C} = f(1/C)$ can be des-

cribed with a straight line only within a certain concentration range (see Fig. 6b). It can be explained by increasing

importance of intramolecular crosslinking (increase in the number of radicals per chain) with decreasing polymer concentration and with increasing dose absorbed after the electron pulse from the accelerator.

CONCLUSION

Oxygen contained in the solution reacts with macroradicals of polyvinylpyrrolidone and results in the scission of the main polymer chain. These reactions have a character of intramolecular conversion, and their slowest stage is the separation of the freshly formed chain fragments (diffusion). For higher polymer concentrations besides the reaction of degradation a process of crosslinking is also observed. It is difficult, on the basis of kinetic experiments, to propose a complete mechanism of crosslinking of PVP in the presence of oxygen. It is however possible to conclude, that this process is caused by the reaction of peroxide macroradicals with the polymer.

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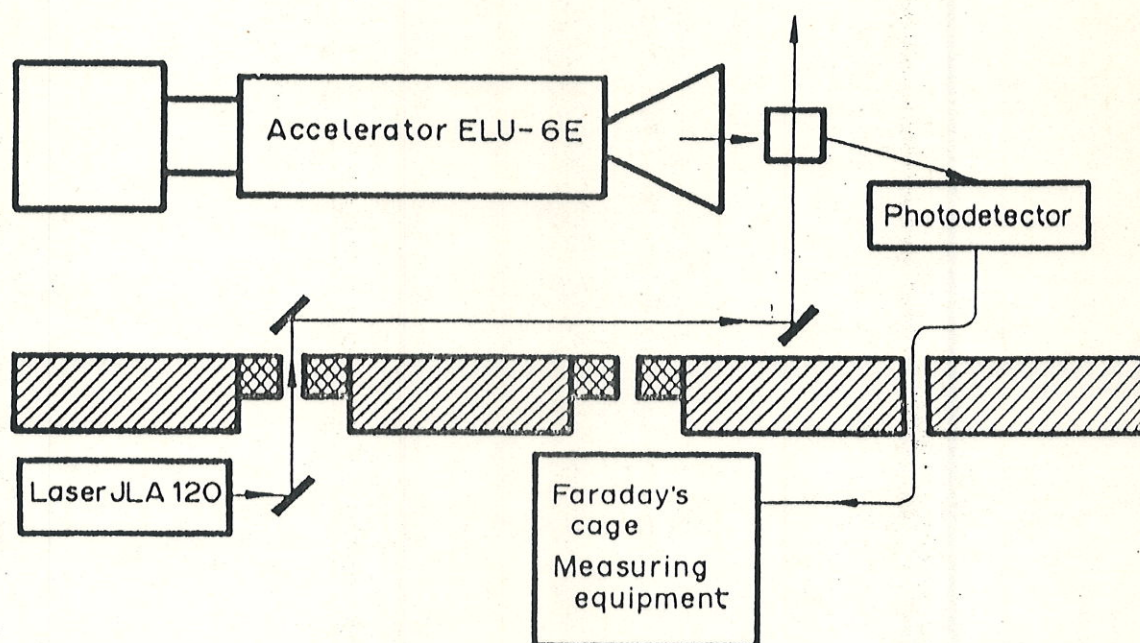


Fig. 1. The layout of LSI system

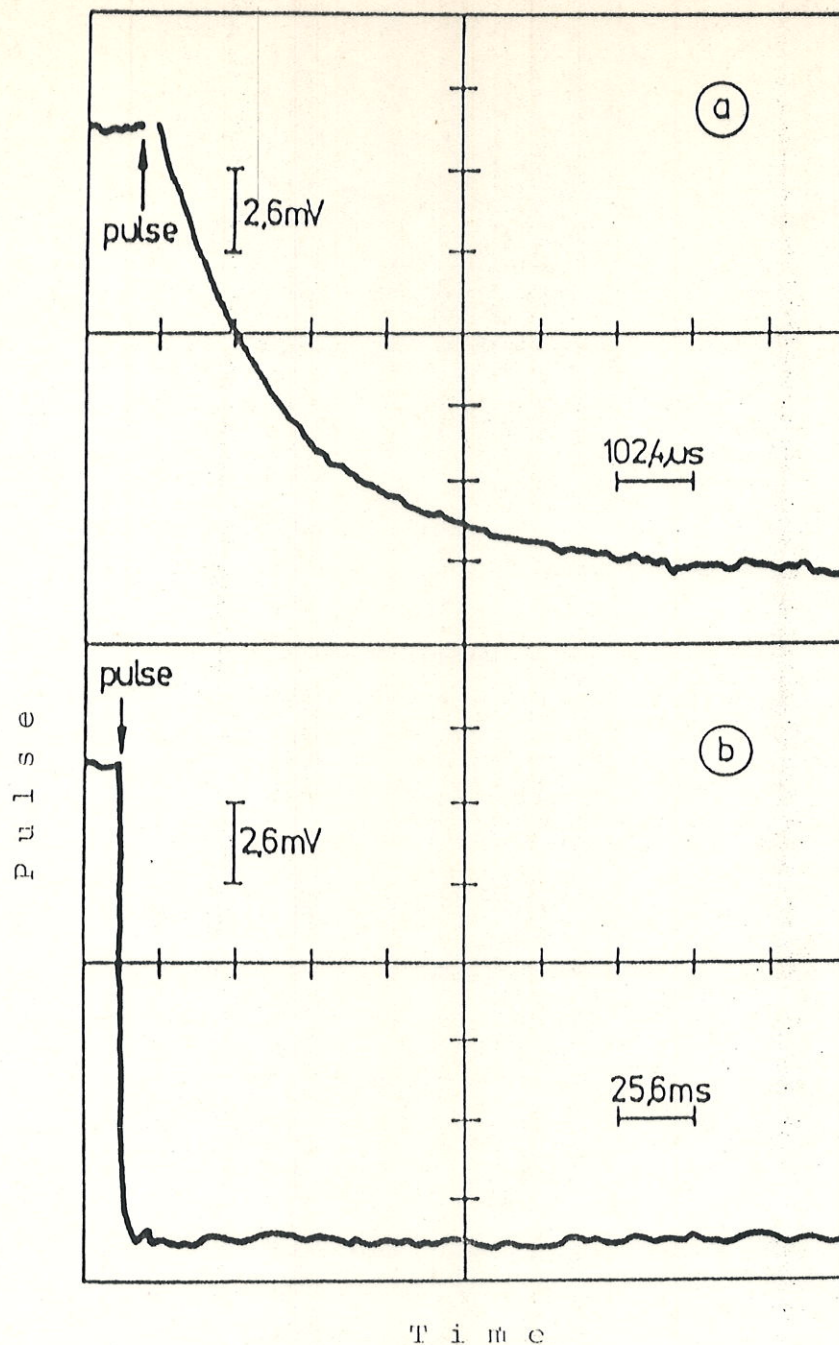


Fig.2. Oscilloscope traces obtained O_2 -saturated aqueous solution depicting the decrease of the LSI; $C_{pvp} = 5.7 \cdot 10^{-3}$ b.mole/dm³; absorbed dose per pulse 0.4 kGy; $U_r = 10$ mV; $U_o = 101$ mV; pulse duration 1 μ s.

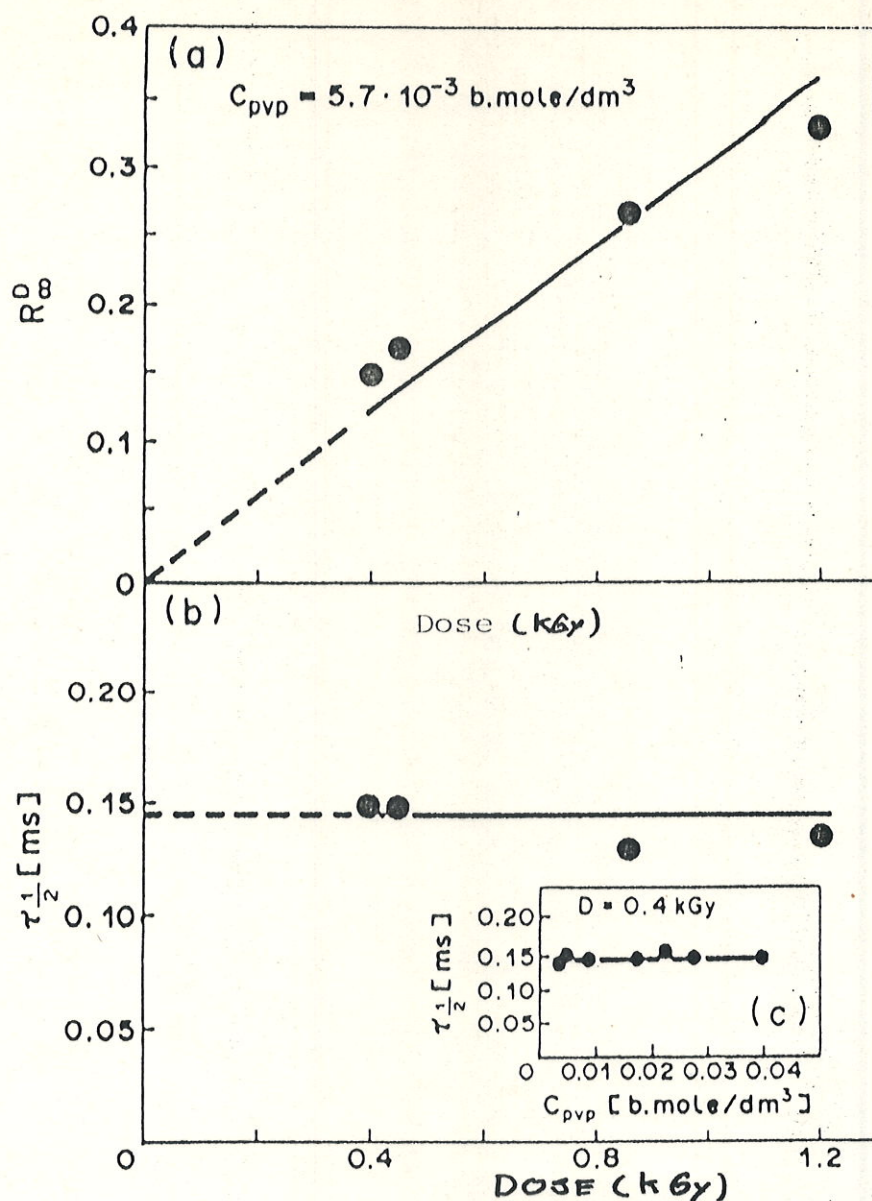


Fig. 3. Main chain degradation of PVP in O_2 -saturated aqueous solution. Total extent of LSI increase (a) and first half-life time as a function of the absorbed dose (b) and concentration of polymer (c).

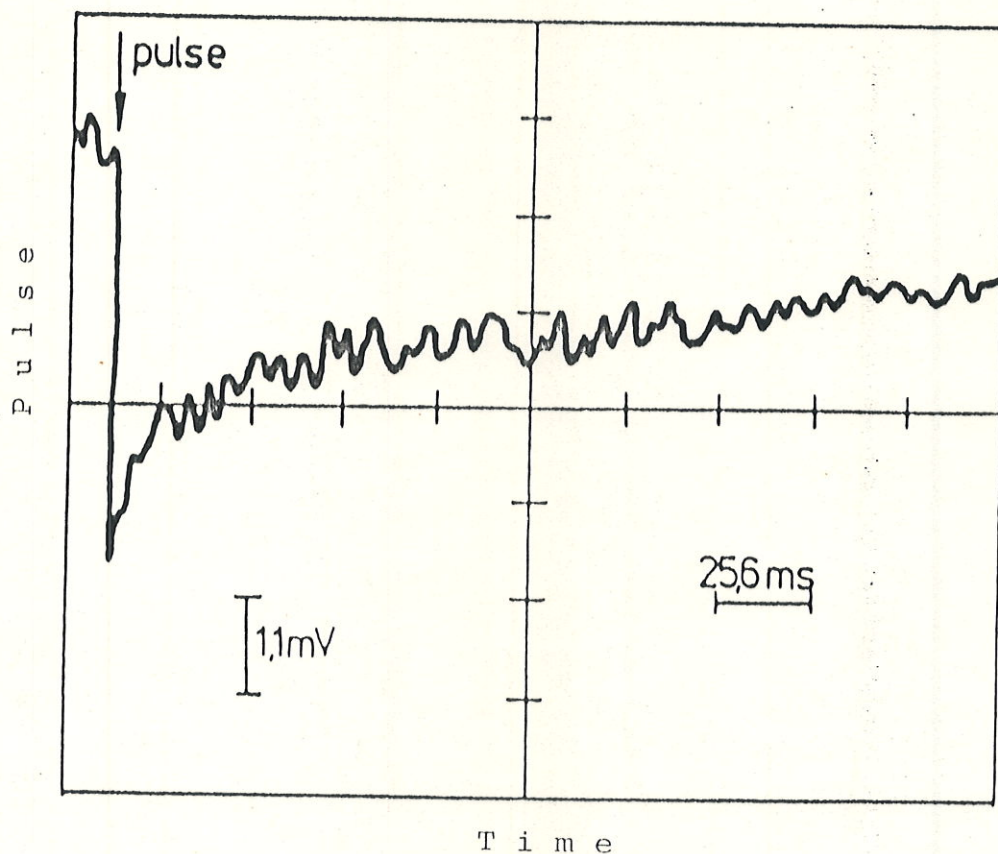


Fig. 4. Oscilloscope trace obtained in O₂-saturated PVP aqueous solution depicting the increase of the LSI; absorbed dose per pulse 0.17 kGy; U_r=9 mV: U_o=181 mV; pulse duration 1 μs. PVP concentration : $\geq 6.2 \times 10^{-2}$ m

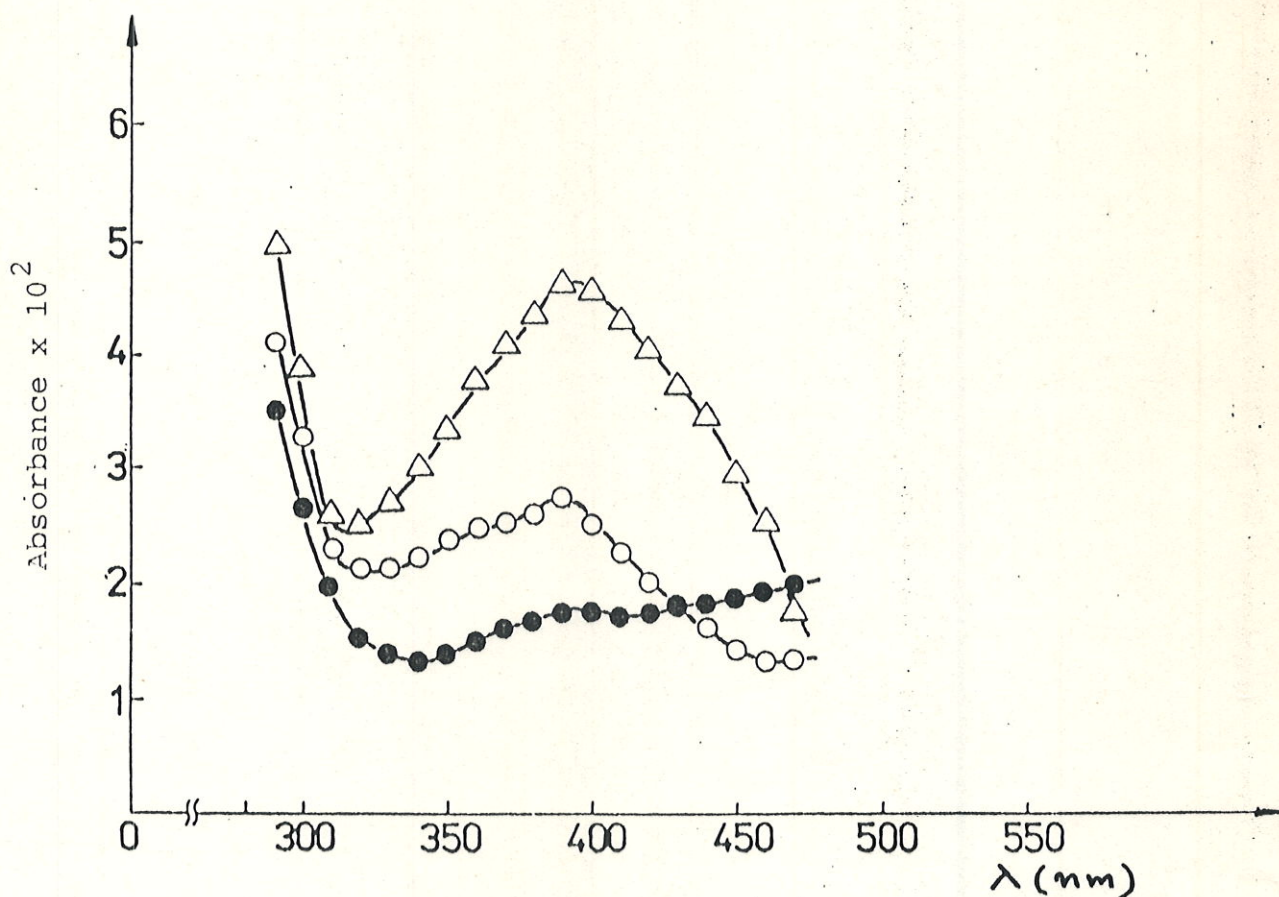


Fig. 5. Absorption spectra of aqueous solutions of PVP immediately after 100 ns electron pulse. The solutions saturated with : O-argon, Δ-nitrous oxide, ●-oxygen. Polymer concentration 1.1. g/dm³

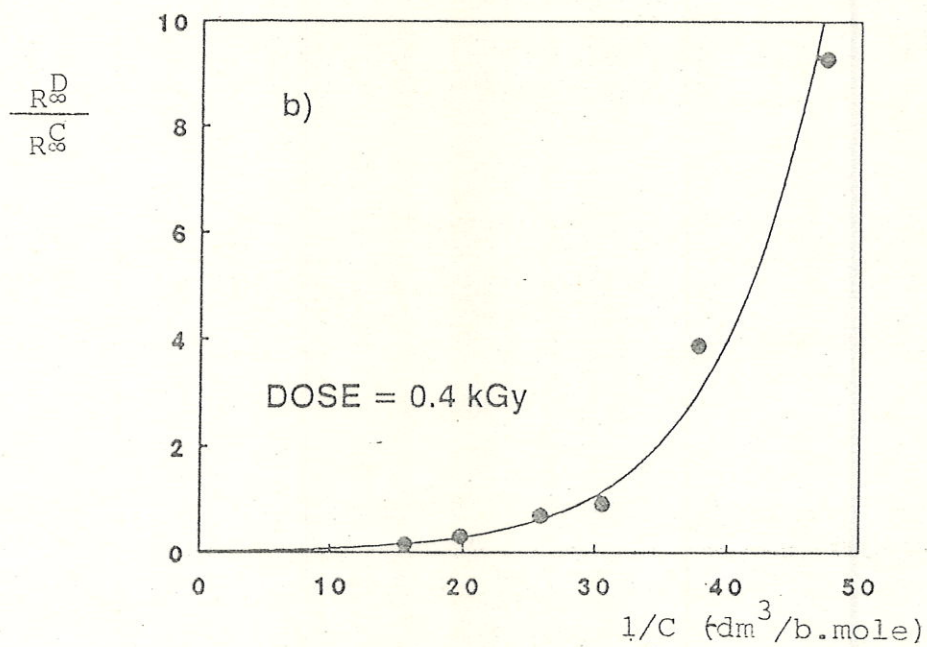
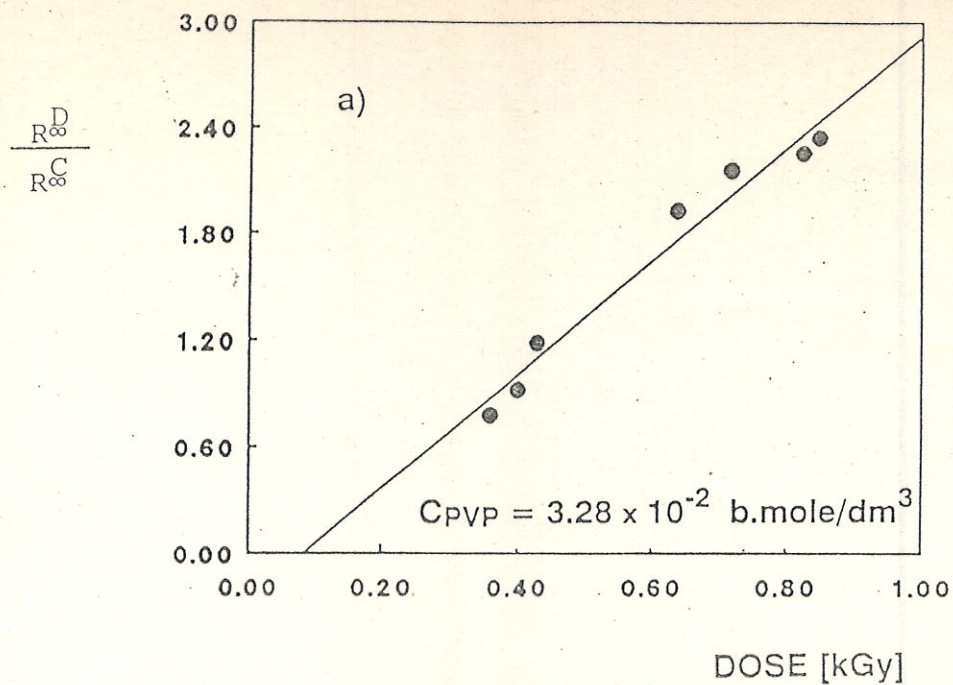


Fig. 6. The ratio of the R_{∞}^D (degradation) to the R_{∞}^C (Crosslinking), PVP in oxygenated aqueous solution.