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Radiation effects and after-effects in the clear polymethyl methacrylate dosimeter



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## Abstract

The irradiation induced optical absorption in clear PMMA has been studied using OD and ESR techniques. The OD-dose relationship has been explained on the basis of radical production and destruction and fragment production and destruction for gamma and fast neutron irradiation. The unstable OD component hes been correlated with the free radical concentration. The photosensitive effect is shown to be caused by a free radical conversion process. The identification of the typical PMMA free radical is considered.

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# **1** Introduction

#### 1.1 Apologia

This thesis is concerned with the investigation of the effect of ionising radiation on clear polymethyl methacrylate (PMMA) and certain after effects occuring in irradiated PMMA using optical and electron spin resonance techniques. The motivation for this work arose from two different considerations. Firstly, clear PMMA, more commonly known under the trade names perspex<sup>1</sup>, lucite<sup>2</sup> and plexiglas<sup>3</sup>, is widely used as a radiation dosimeter in the dose range 100 krad to 10 Mrad in which the radiation induced optical density change is used as a measure of the dose. This radiation induced optical density change is not completely stable and is dependent upon certain environmental factors. An investigation into the processes involved in the stability of the radiation induced effect is relevant to the use and accuracy of clear PMMA as a radiation dosimeter. Secondly, in the development of a programme, concerned with the study of primary radiation effects in biochemicals using optical and electron spin resonance techniques at the Institute for Atomic Sciences in Agriculture, Wageningen. the Netherlands, it was considered useful to gain experience and insight into the possibilities and problems associated with the combined use of these techniques. It was decided that polymethyl methacrylate, a long chain high molecular weight organic molecule would be a suitable model for biochemicals and an ideal practical material.

PMMA is readily available in a reproducible relatively pure form, degrades on irradiation and does not crosslink, and has often been used in irradiation studies.

- (1) manufactured by I.C.I. Ltd., Welwyn Garden City, England
- (2) manufactured by E.I. du Pont de Nemours and Co. Ltd., Wilmington, U.S.A.
- (3) manufactured by Röhm and Haas GmbH, Darmstadt, W. Germany

#### 1.2 Literature review

The radiation studies using PMMA of greatest relevance to the work presented in this thesis may be conveniently divided into two parts: those concerned with the use of the polymer for radiation dosimetry applications using a measure of the change in optical density (OD) as representative of the radiation dose, and those concerned with the identification of the free radical products of the irradiation using electron spin resonance (ESR) techniques.

1.2.1 Optical measurements on irradiated clear polymethyl methacrylate

In 1951 two related papers were published by Day & Stein, and by Schneider et al., which discussed the effects of X-rays on plastics and considered the change in optical density of clear and coloured PMMA and the induced paramagnetic resonance in clear and coloured PMMA and polystyrene. A relationship between the two phenomena was found, and both were ascribed to the trapping of electrons at defects in the polymer lattice in the same way that colour centres in inorganic crystals formed by trapped electrons also give a paramagnetic resonance. In 1955, Fowler & Day published a paper on the use of clear PMMA and polystyrene to measure large radiation doses using optical density techniques. PMMA was found suitable for doses in the range  $10^6$  to 5 x  $10^7$  rads, and the fading of the OD with storage time was associated with the diffusion of oxygen into the polymer matrix.

Boag et al. (1958) presented a more basic paper on the use of clear PMMA for radiation dosimetry and studied the effects of various environmental factors on the reproducibility of the results. Water absorption and mechanical stress had no measurable effect, heat treatment at  $110^{\circ}$ C gave different results, at low doses the OD increased, at high doses the OD faded, no dose rate effect was found up to 3 x  $10^{8}$  rad/s. The effect of contaminants normally found in PMMA was negligible except for a sample containing dibutyl phthalate as plasticiser, which had a strong green colour immediately after irradiation due to an absorption band at 800 nm which faded very rapidly and was not important after 2 hours. Boag et al. also associated the slow fading in irradiated PMMA with the diffusion of oxygen into the plastic matrix. An optical density - dose calibration curve was presented which showed that at low doses the curve was non-linear, and it was suggested that the low sensitivity over the first  $10^{5}$  rads may be associated with the presence of oxygen in the matrix prior to irradiation, the normal sensitivity being achieved when the oxygen had been burnt up. At doses above 3 Mrad the OD-dose relationship became sub-linear.

The effect of different amounts of polymerisation initiator and monomer on the radiation induced OD was studied by Orton (1966). He found that the initiator, benzoyl peroxide, was responsible for the strong optical absorption between 250 nm and 300 nm in the untreated PMMA, and that the amount of initiator apparently affected the rate of fading when irradiated samples were stored in air. On extended storage in air, a stable value of the OD was found and the fading in air proved to be dependent on wavelength, between 280 nm and 320 nm the OD initially increased, often dramatically, before eventually fading. The decrease of the OD on storage in air was found to be diffusion controlled and almost certainly due to oxygen. The effect of monomer was less important, although increasing amounts of it did increase the OD at wavelengths above 280 nm after irradiation. The monomer had no effect on the fading. As a result of this work a formulation was made for a PMMA which would have optimal properties for use as a radiation dosimeter; a large amount of this PMMA has been manufactured by I.C.I. Ltd., Welwyn Garden City, England, under the trade name HX-dosimetry perspex for the U.K. Panel on Gamma and Electron Irradiation (Orton & Berry, 1966).

One experimental factor which Orton did not control, and which indeed had not been considered by any of the previous workers in this field, was light. The importance of this factor was revealed in 1967 in a paper on the photosensitivity of irradiated clear PMMA (Whittaker & Lowe, 1967). Although the paper was not very explicit about the light exposures of the PMMA, the results were important enough to illustrate that exposure of irradiated clear PMMA to normal sunlight for one day could change the OD at 292 nm by as much as 50 %.

In 1969, two independent papers, by Chadwick and by Berry & Marshall, discussed the practical problems involved in the use of clear PMMA for radiation dosimetry. An important feature of both papers is a proposal to work at a different wavelength than that which had previously been used, namely 292 nm. Chadwick proposed 314 nm to be more sensitive for low dose measurement and to be relatively stable for temperature variations below  $60^{\circ}$ C and under normal light conditions in a laboratory. Berry and Marshall proposed a change in wavelength, because the peak in the induced OD spectrum, previously measured at 292 nm, was found to be an artefact caused by stray light conditions in the measuring spectrophotometers and the optical

absorption cut off occurring in the unirradiated PMMA at 290 nm. The wavelength 305 nm was chosen by them because it gave a more sensitive response than 292 nm and because it was the same wavelength as used for the Fricke ferrous sulphate dosimeter which is normally applied as a standard dosimetry system. Chadwick showed that by pretreating the PMMA to remove the oxygen, an OD-dose relationship could be obtained which was linear from the origin and in doing so, justified the proposal of Boag et al. (1958) that the non-linear low dose portion of the curve was due to oxygen present in the matrix. It was also shown that on exposure to intense light, the OD not only increased dramatically but also bleached. Both papers concluded with a series of practical rules which should be followed if meaningful results were to be obtained. These rules are summarized here because the same phenomena of photosensitivity and fading can also affect the measurements which form the basis of this thesis.

- 1. The material should be carefully cleaned before use.
- 2. Pre-irradiation background measurements should be made on the samples, or measurements should be made against a suitable control sample.
- 3. Exposure of samples to light during or after irradiation should be avoided.
- Measurements should be made within a few hours of the irradiation unless special storage conditions are provided, i.e. vacuum and darkness at about 10°C.
- 5. For long irradiations PMMA should be kept under vacuum to avoid oxygen diffusion induced fading of the signal.
- 6. Temperature's above 60°C should be avoided during and after irradiation.
- 1.2.2 Electron spin resonance measurements on irradiated polymethyl methacrylate

In the field of free radical studies in PMMA using electron spin resonance techniques the nine line spectrum found originally by Schneider et al. (1951) has become the subject of considerable discussion as its indisputable identification has not yet been possible. It is generally agreed that the normal nine line spectrum is, in fact, made up of a five line spectrum which has a weaker four line spectrum superimposed on it.

The original proposal by Schneider et al. that the spectrum arose from trapped electrons was quickly overruled and Abraham et al. (1958) found that the five line A set spectrum had intensities of 1 : 4 : 6 : 4 : 1 and

the four line B set spectrum had intensities of 1:3:3:1 but was much weaker than set A. On irradiation of other comparable materials they found that similar spectra were formed and concluded that the main chain of the polymer was essential to the nine line spectrum. In identifying the spectrum they considered the possibility that it was formed by two distinct radical species, but after discussing many alternatives rejected the proposal in favour of a single radical

$$R - CH_2 - C \cdot |$$

$$COOCH_3$$

(1)

which would have two different configurations, and thus the different intensities of the five line A set and four line B set would reflect the relative probabilities of the two structures. Abraham et al. also considered why this radical appeared to be the only one when simple chain breaks would leave an equivalent number of radicals with the form

 $R - \dot{C}H_2$ 

They considered that this radical might attack the normal polymer chain or react with excess monomer to produce the original radical. In either case their proposal of chain rupture is consistent with the finding that chain degradation and not cross linking is the main effect of radiation on PMMA (Ormerod & Charlesby, 1964).

In 1959, Symons proposed a theory which accounted for a nine line spectrum arising from the radical 1, albeit with intensities which did not completely agree with those already found. In 1963 he revised this theory and discussed the alternative proposal of two radical species. He showed that his explanation for the spectrum satisfied the experimental findings which were used to support the two radical theory. He modified his theory to account for the difference between the predicted and the measured line intensities.

In an extremely elegant paper, describing electron spin resonance measurements on deuterated polymethyl methacrylate, Kourim & Vacek (1965) showed that one of the interpretations of Abraham et al. (op. cit.) was

wrong and that the proposal of Bullock & Sutcliffe (1964) that the four line B set spectrum arises from the radical

$$CH_{3}$$

$$|$$

$$CH_{2} = C - \dot{C}H$$

$$(2)$$

and the five line A set spectrum from radical 1 in a special configuration was not borne out in the deuterated PMMA spectra. On the contrary, the results favour very strongly the proposals of Symons.

Fischer (1964) studied polymerisation radicals of methacrylic acid in liquid samples which gave an improved resolution and found a sixteen line spectrum closely resembling the nine line spectrum in intensity and splitting. He concluded that in rigid samples anisotropy broadening prevented the resolution of the splittings within the nine lines, and that the nine line spectrum was the polymerisation radical. He also concluded that the measured sixteen line spectrum was in agreement with the proposals of Symons.

In further support of the proposal that the nine line spectrum arises from one radical, Michel et al. (1967) showed that the decay of the spectrum at elevated temperatures, where the five line spectrum had been found to decay at a different rate than the four line spectrum, could be accounted for if the nine line spectrum was considered to be super-imposed on a small broad singlet spectrum, which was relatively temperature stable and which peaked by the four line spectrum, and did not contribute to the five line spectrum. In this way they found that the decay of both the five and four line spectra was identical and consequently suggested that they both arose from one and the same radical.

The evidence which has been presented in favour of two different radical species being superimposed to make up the nine line spectrum, arises mainly from studies on the effect of warming on the shape and decay of the nine line spectrum. Campbell & Looney (1962), studying the decay of the free radical spectrum at elevated temperatures, found two different decay rates and modes for the five and four line spectra and concluded that two different radicals were present.

Ormerod & Charlesby (1964), in an extensive study mainly concerned with low temperature irradiations, ESR spectra and the different intermediate reactions, also mentioned the probability of two different radical species forming the nine line spectrum.

The paper of Bullock & Sutcliffe (1964) presents the only serious argument in favour of the formation of two radical species. They used four methods to produce radicals in PMMA and found some differences in the resulting spectra; in addition they studied the fading of the spectra at elevated temperatures. They proposed that the five line spectrum arises from radical 1 and that the four line spectrum arises from radical 2, but their arguments against the proposals of Symons are not convincing, and a careful examination of the different spectra in their paper suggests that their results could be explained equally well on the basis of a broad singlet, superimposed on the nine line spectrum, as has been proposed by Michel et al. (1967) to explain the results of Campbell & Looney (1962). If this is the case, it would have to be assumed that the relative importance of the singlet and nine line spectrum would be influenced by the method of production of the free radicals. If this is so, the discrepancy between the different results and opinions would be resolved so that the free radical spectrum would no longer be made up of a five line plus a four line set but would be a nine line spectrum ascribed to radical 1 superimposed on a broad singlet spectrum which is as yet unidentified. Several publications mention or show the singlet spectrum (Ormerod & Charlesby, 1964; Michel et al., 1967), Ohnishi & Nitta (1959) state that at radiation doses above 50 Mrad the ESR spectrum is a broad singlet with only a slight indication of fine structure.

#### 1.3 Experimental techniques

In the work presented here, three experimental techniques have been used, and attempts have been made to correlate results from the different techniques in order to obtain, with a broader scope, a more detailed picture of the events taking place. The techniques which have been used in this investigation are optical density (OD), electron spin resonance (ESR) and photoluminescence (PL).

#### 1.3.1 Optical density measurements

If a molecule absorbs energy in the near ultra-violet (200-400 nm), changes in the electronic, vibrational and rotational energies will take place. The ultra-violet absorption spectrum of a molecule is thus more complicated than the rotational or rotational-vibrational spectrum, and

the different sub-levels will be so closely spaced that the ultra-violet spectra of polyatomic molecules will appear as broad absorption bands or band envelopes. The complex nature of the electronic spectra of polyatomic molecules is almost impossible to analyse completely.

The optical density is defined by the Beer-Lambert Law of light absorption which states that 'the fraction of incident light absorbed is proportional to the number of molecules in the path' and may be expressed as

optical density = 
$$\log_{10} \frac{I_0}{I} = k N t$$

where in this case  $I_0$  is the light intensity with an unirradiated sample in the light path, I is the light intensity with an irradiated sample in the light path, N is the number of radiation induced absorbers, k is related to the extinction coefficient of the absorber, and t is the path length in the sample.

The work of Dole & Böhm (1966) is a good example of the use of optical absorption measurements for the study of radiation products in a polymer. Working with polyethylene at room temperature and later at  $77^{\circ}$ K, they were able to identify several radiation products positively and to suggest possible identifications for other species.

## 1.3.2 Electron spin resonance measurements

For a comprehensive treatment of the ESR process the reader is referred to the book "Electron Spin Resonance" by C.P. Poole (Interscience publishers 1967). The process may be described simply as follows:

If unpaired electrons are placed in a steady magnetic field  $H_0$ , the dipole moment  $\mu$  of the electrons will precess about  $H_0$  with a characteristic angular velocity  $\omega$  where

 $\omega = \gamma H_0$ 

and  $\boldsymbol{\gamma}$  is known as the gyromagnetic ratio.

This Larmor precession is a passive process and does not lead to the detection of the unpaired electron. If a second, alternating magnetic field  $H_1$  is provided at right angles to  $H_0$  then the motion of the dipole of the unpaired electron is disturbed, and when the frequency of the alternating magnetic field is equal to the precessional frequency of the dipole, a

resonance transfer of energy occurs between the energy source  $H_1$  and the dipoles, even if  $H_1 << H_0$ . This resonance energy absorption is observable and is the basis of electron spin resonance spectrometry.

The quantum energy of the micro-wave field providing the alternating magnetic field is  $h\nu$  and the condition for resonance is

 $hv = g \beta H_0$ 

where g is the spectroscopic splitting factor,  $\beta$  is the Bohr magneton, and  $H_0$  is the d.c. magnetic field.

The spectroscopic splitting factor g is a property of the unpaired electron in its environment. The hydrogen atoms have a magnetic nucleus which will be affected by the magnetic field  $H_0$ , and each hydrogen nucleus will be oriented either parallel or anti-parallel to  $H_0$ . These nuclei produce a magnetic field of their own and this field, together with  $H_0$ , comprises a modified field which is actually experienced by the unpaired electron. This interaction of the unpaired electron and the hydrogen nuclei leads to the hyperfine splitting and resonance absorptions displaced from the position of symmetry of the spectrum. The number of resonance absorption lines in a spectrum will depend on the number of hydrogen nuclei coupling with the unpaired electron, and on the number of the lines will depend on the number of permutations of the hydrogen nuclei which can lead to the specific arrangements. Thus the ESR spectrum characterizes the free radical and can consequently be used to identify it.

Electron spin resonance has been used to study radiation effects in hundreds of materials (Ingram, 1958; Gordy, 1961; Smith, 1962; Zimmer, 1962; Zimmer & Müller, 1965). Recently, Keyser et al. (1968) and Keyser & Williams (1969) have presented both ESR and optical absorption evidence for the occurrence of trapped electrons in polymers irradiated at low temperatures.

#### 1.3.3 Photoluminescence measurements

When a molecule is raised from the ground level S to an excited state  $S^1$  by light absorption, it undergoes de-activation by collision with other molecules and emission of radiation takes place when it reverts from the excited state  $S_1$  to the ground state. This emission process is called luminescence; when it occurs via the absorption of light, it is called

photoluminescence or optically stimulated luminescence. If the de-excitation occurs via a direct transition from the singlet state  $S_1$  in a very short time ( $10^{-9}$  sec), the phenomenon is known as fluorescence; when it occurs through an intermediate triplet state  $T_1$ , of lower energy than  $S_1$ , the life time in the excited state being long (>  $10^{-3}$  sec), the phenomenon is known as phosphorescence.

Photoluminescence as a technique on its own does not appear to have been used extensively for the study of irradiated organic materials (Goedbloed & van Hemmen, 1969), although it has long been used as a system of radiation dosimetry (Becker, 1966). Fluorescence and phosphorescence techniques have been used to examine organic chemicals (Longworth, 1968) and to study energy transfer mechanisms and bond structure. The photoluminescence of irradiated PMMA was first mentioned by Dészi et al. in 1966.

## 2 Methodology

### 2.1 Radiation facilities

Irradiations have been made in several facilities, mostly for the sake of practical convenience, using gamma-rays from  $^{137}$ Cs and  $^{60}$ Co, 1.5 MeV electrons from a Van de Graaff electron generator and the Bremsstrahlung from the same machine fitted with a gold target. In order to study the effect of radiation of a different LET, irradiations have also been made in the fast neutron field of the BARN reactor.

#### 2.1.1 Gamma ray sources

A 5000 Ci  $^{137}$ Cs (0.66 MeV,  $_{\rm Y}$ ) source made up of two units, each of 2500 Ci has been used such that the dose rate at the irradiation position was 860 rad/h ± 2 % with a vertical uniformity of 3 % over a height of one metre. A high dose rate modification of the 5000 Ci source has also been used. A unit having fourteen turntables was fitted to the source guide tube opposite one 2500 Ci source. The turntables are driven continuously during exposure to ensure a homogeneous irradiation. The dose rates measured on the different turntables varied from 214 krad/h for the closest to 25 krad/h for the one farthest from the source.

Irradiations have been made in the  $^{60}$ Co (1.17, 1.33 MeV,  $\gamma$ ) Gamma Cell 2000 (Atomic Energy Commission Canada Ltd.) at the Radiobiophysics Department of the University of Utrecht. Samples were irradiated in the centre of the field only, and were held in position by a Styrofoam template. The dose rate of the facility was measured with the Fricke ferrous sulphate dosimeter and found to be 560 krad/h ± 3 % at the centre of the facility at the time of irradiation.

#### 2.1.2 Electron and Bremsstrahlung sources

Electron irradiations have been made using a 1.5 MeV Van de Graaff.

The maximum current of this generator is 1.5 mA and because the machine is used for food irradiation studies the electron beam is scanned electromagnetically in one direction (x) at 200 Hz over 38 cm at the beam exit window, and the sample is passed through the beam in the y direction. Different doses were given to the sample by either controlling the beam current or by a multiple pass through the beam. In order to avoid the creation of 'Lichtenberg patterns' or 'trees', which occur readily in PMA4 under electron irradiation, the dose rate was kept as low as possible (2.5 x  $10^5$  rad/s). Normally, the lower limit of the dose rate is determined by the column current, that is the current which is present when there is no beam. The minimal total current must be taken as at least twice the column current so that slight variations in the column current do not seriously affect the reproducibility of different irradiations.

In later experiments use was made of a system, developed at the Institute for Atomic Sciences in Agriculture, to avoid this low beam current reproducibility problem which has been called the 'electron-copter'. The electron-copter is made up of two small pick-ups at each end of an arm which is rotated at its centre point, which in turn is fixed at one end of the beam scanner. Measurements are made of the peak current as the pick-up passes through the electron beam. This value is displayed and held on a digital voltmeter until the second pick-up passes through the beam and the machine can be controlled on these readings. The frequency governing the rotation of the pick-ups is derived from the scan frequency and the pick-up is shielded from backscatter to avoid interference caused by the passage of different samples through the beam. The speed of rotation has been chosen so that the pick-up is only in the beam for 2 % of the time that a sample is in the beam and the reproducibility of consecutive measurements is ± 1 %. Thus the electron-copter enables controlled and reproducible low dose rate electron irradiations to be made.

Some low temperature electron irradiations were made with the PMMA samples placed on a copper plate welded to a copper rod submerged in liquid nitrogen in a dewar. The samples and copper plate were surrounded by styrofoam plastic to provide insulation. The temperature measured in a sample of PMMA on this plate was  $-160^{\circ}$ C. This temperature is critical for PMMA irradiation as it has been found that the thermoluminescence glow peak in low temperature irradiated PMMA occurs at  $-160^{\circ}$ C and therefore quantitative measurements have been made using the variable temperature unit (see section 2.4.4).

Some irradiations have been made using the Bremsstrahlung arising when a gold target is placed over the electron window of the 1.5 MeV Van de Graaff accelerator. The dose rate of this radiation field has been determined using the Fricke ferrous sulphate dosimeter. The machine is invariably run at full power of 1.5 MeV and 1.5 mA for these irradiations.

## 2.1.3 The BARN reactor

The 100 kW BARN tank type reactor (Bogaart et al., 1964) has as its main facility an irradiation room situated under the reactor core and separated from it by a  $D_2O$  diffusor (Fig. 1). A fast neutron beam may be obtained in the irradiation room by dumping the  $D_2O$  from the diffusor. Two bismuth shields, totalling 17.5 cm of bismuth, are situated under the  $D_2O$  tank to attenuate the core gamma rays. The thermal neutron contamination of the fast neutron beam is reduced by placing a boron layer between the two bismuth gamma shields.



Fig. 1 Vertical cross section of the BARN reactor.

## 2.2 Radiation dosimetry

The calibration of the different systems used for radiation dosimetry in the various facilities has been achieved using a secondary standard dosimeter, the Fricke ferrous sulphate dosimeter.

### 2.2.1 Calibration of the Fricke ferrous sulphate dosimeter

Irradiation of the Fricke dosimeter induces the oxidation of the ferrous ion to ferric. The ferric ion can be determined spectrophotometrically and in the range 0 to 40 krad the concentration of ferric ion is directly proportional to the radiation dose. The response of the dosimeter has been compared with calorimetric determinations of the radiation dose in an electron beam.

The Fricke dosimeter was made up to the formulation of Weiss et al. (1955): 2 gm  $\text{FeSO}_4.7\text{H}_2\text{O}$  or  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2.6\text{H}_2\text{O}$  and 0.3 gm NaCl was dissolved in 110 cc (95 - 98 %) concentrated  $\text{H}_2\text{SO}_4$ ; the acid was diluted with sufficient doubly distilled water to make 5 litres of solution. All chemicals were analytical reagent grade.

The molar extinction coefficient of the ferrous sulphate solution was determined using the method of Holm et al. (1961): 0.135 gm (about  $\frac{1}{3000}$  mole) of Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O was dissolved in 0.5 litre of 0.8 N H<sub>2</sub>SO<sub>4</sub> and between 2 and 4 cc of perhydrol (30 % solution of H<sub>2</sub>O<sub>2</sub>) was added and the solution was boiled under reflux condensation for one hour. After cooling to room temperature the solution was poured into a 1 litre volumetric flask and 0.8 N H<sub>2</sub>SO<sub>4</sub> was added to just under the volume mark. The flask was then thermostated at 25°C for one hour and 0.8 N H<sub>2</sub>SO<sub>4</sub> was added up to the 1 litre mark. Using this solution the peak of the optical absorption curve was found at 304 nm and all other optical measurements were made at this wavelength. The temperature dependence of the extinction coefficient was measured and found to be 0.8 % per °C. The molar extinction coefficient found using this method was

The calorimetry system was made up of two identical graphite discs, one to measure the ambient temperature, the other to measure the radiation. Thermistors were used in conjunction with a Wheatstone bridge amplifier network to measure the temperature change caused by radiation. The thermistors were embedded in the graphite discs in such a position, with respect to the Bragg curve, that they measured only the mean temperature of the graphite. The thermal insulation of the calorimeters was achieved using styrofoam; the high beam intensities used in the experiment obviated the need for vacuum insulation techniques.

Calibration of the calorimeters was achieved by passing a known electric current directly through the graphite for an accurately controlled time which was identical to the radiation exposure time. The energy of the electron beam was adjusted until all the electrons were just totally absorbed in the graphite. After irradiation the cooling rate of the calorimeter was found to be different than that found after the electrical heating and an appropriate correction of 1.7 % was applied to the energy measurement.

Irradiation of the Fricke dosimeter was made using perspex containers with a cross section equal to that of the graphite calorimeter. The calorimeter and the Fricke dosimeters were passed along the same path under a broad slit through a constant electron beam, using a turntable driven by a synchronous motor. During the run-up and run-down of the electron generator the dosimeters and calorimeter were shielded.

The value for  $G_{Fe}$ , the number of ferrous ions converted to ferric ions per 100 eV absorbed energy, was calculated using the equation:

$$G = \frac{9.65 \cdot 10^8 \cdot \Delta OD}{\epsilon \cdot d \cdot D \cdot \rho}$$

- where  $\Delta$  OD is the difference in OD at 304 nm and T<sup>O</sup>C between irradiated and unirradiated Fricke solution,
  - $\varepsilon$  is the molar extinction coefficient of the Fricke solution at 304 nm and T<sup>O</sup>C,
  - d is the path length of the sample used in the OD measurement,
  - D is the radiation dose,

and  $\rho$  is the density of the Fricke solution. The value found was  $G_{E_{P}} = 15.88 \pm 2$  %.

This value is some 1.5 % higher than those mentioned in literature (Spinks & Wood, 1964; Fregene, 1967; Ahmed et al., 1970), but on the other hand the value of the extinction coefficient quoted here is some 3 % lower than those found in literature (Law, 1970). It has been found that the extinction coefficient can vary from spectrophotometer to spectrophotometer (Law, op. cit.) by as much as 2 %, which does not explain the total dis-

crepancy found here. However, the high G value may to some extent be a result of the too low extinction coefficient.

In a measurement made in the gamma cell at the Radiobiophysics Department of Utrecht University the dose rate found, using the Fricke dosimeter with the values quoted, agreed to within 3 % with the dose rate measured in the same facility by the Radiobiophysics Group. Thus, it seems reasonable to assume that dose rate measurements carried out using the Fricke dosimeter with the values quoted here, are accurate to within 3 % and that doses arising from these measurements are accurate to within 5 %.

#### 2.2.2 Electron dosimetry

Dosimetry of the electron beam was carried out in the different experimental arrangements using clear polymethyl methacrylate at room temperature, which had previously been calibrated against the Fricke ferrous sulphate dosimeter in a gamma ray field. Berry & Marshall (1969) state that the difference between electron and  $\gamma$  radiation results are small for 1 mm material at doses below 3 Mrad. In this work, 2 mm thick PMMA has been used but the errors made in the use of a gamma calibration curve for electron dosimetry are most probably negligible. More important is the fact that with 2 mm PMMA and 1.5 MeV electrons it was impossible to achieve a uniform dose distribution and the dose measurements must be considered as a mean value with a distribution through the PMMA sample of plus and minus 10 %.

## 2.2.3 Fast neutron spectrometry and dosimetry

The fast neutron spectrum and dose rates have been measured in the reactor irradiation facility and the kerma rate, calculated from the spectrum, has been compared with the dose rate measured using ionization chambers (Chadwick et al., 1968; Chadwick & Oosterheert, 1969).

The neutron spectrum was measured with a semiconductor sandwich detector making use of the following reaction:  ${}^{6}\text{Li}(n,\alpha)\text{T}$ ; Q-value 4.78 MeV. The pulses resulting from the charged particle interaction with the semiconductors were processed in a sum-coincidence system and the sum pulse was stored in a 400 channel analyser opened by a coincident gate pulse. The pulse height spectrum was corrected for detector efficiency and grouped in energy intervals of 280 keV to give the fast neutron spectrum (Fig. 2).

The neutron dose rate was measured using an acetylene equivalent ioni-



Fig. 2 The fast neutron spectrum measured in the sub-core irradiation room of the BARN reactor.

sation chamber and a magnox argon ionisation chamber was used to measure the gamma ray contamination. Calibration of the ionisation chambers was made against the Fricke ferrous sulphate dosimeter using the 5000 Ci  $^{137}\mathrm{Cs}$  source.

In the calculation of the neutron dose rate a dependence of W, the energy needed to create an ion pair in a gas, on the specific ionisation density of the radiation was assumed (White, 1963). The values are given in Table 1.

Table 1. The values of W used to estimate the fast neutron dose rates from ionisation chamber measurements				
	Acetylene C <sub>2</sub> H <sub>2</sub>	Tissue equivalent gas 64.2 % CH <sub>4</sub> , 32.5 % CO <sub>2</sub> , 3.3 % N <sub>2</sub>		
Wy Wp	25.7 27.5	29.4 31.0		

The kerma rate was calculated from the fast neutron spectrum using the kerma factor for tissue equivalent plastic (Williamson & Mitacek, 1966). The dose rate obtained from the acetylene equivalent chamber was corrected by a factor 1.23 to arrive at the tissue equivalent dose rate (IAEA, 1967). Table 2 gives a compilation of dose rates measured by and calculated from the different systems in the calibration position.

Table	2.	Compari	ison	of	the	fast	neutron	dose	rates	measured
with	ioni	sation	chan	nber	(s ai	nd ca	lculated	from	the s	pectrum

	Spectrometer	Ionisation chambers			
		1.23 x CH	T.E. muscle		
Dose rate in T.E. Muscle, rad/h	1100 ± 10 %	1140 ± 7 %	1140 ± 7 %		

The neutron dose rate in polymethyl methacrylate can be calculated from the value measured with the acetylene equivalent chamber using the atomic composition of PMMA ( $CH_2$  :  $C(CH_3)COOCH_3$ ) and the data presented in Table 3.

Table 3. Contribution to neutron dose rate per weight percentage of element relative to dose rate in acetylene

Element	Neutron dose rate		
Н	0.112		
С	0.0015		
0	0.0012		
N	0.0014		

Thus  $D_{PMMA} = (8 \times 0.112 + 60 \times 0.0015 + 32 \times 0.0012) D_{CH} = 1.024 D_{CH}$ .

## 2.3 Materials

Two different types of commercially available PMMA have been used for the measurements discussed here: P1 type of PMMA contains < 0.5 aliphatic peroxide initiator, 1 dibutyl phthalate plasticiser and < 1 monomer; P2 type of PMMA contains < 0.5 aliphatic peroxide initiator, no plasticiser and < 1 monomer. These contaminants were quoted by the manufacturer who was reluctant to give more details and who asked to remain anonymous.

The initiator is used to start the polymerization from the monomer and forms the end groups of the polymer chain (Kinell, 1959). The penetration of plasticiser in a polymer matrix increases the average distance between the polymer chains and segments gain more volume for thermal fluctuations (Fujita & Kishimoto, 1958).

The density of the material was 1.18 gm/cc. All PMMA samples were washed in Alconox detergent rinsed and dried prior to measurement. In dose measurements the initial OD of the samples was measured before irradiation and thickness corrections were made where necessary. In OD spectrum measurements the irradiated sample was compared against an appropriate unirradiated sample in a double beam spectrophotometer.

In some experiments the PMMA samples have been pretreated by heating to  $130^{\circ}$ C under a vacuum (0.5 mm Hg) for between 7.5 and 10 min. for P1 and 15 and 20 min. for P2. This pretreatment removes the molecular oxygen which is normally present in the PMMA matrix.

A review of the literature reveals that in the OD field the same form of irradiated induced OD spectrum has been found in different sorts of PMMA. Boag et al. (1958), Orton (1966) and Berry & Marshall (1969) in particular used a PMMA which was initiated by benzoyl peroxide and which did not contain any plasticiser. In the field of ESR measurements the well known nine line spectrum has been found both in commercial and specially prepared samples of PMMA. Thus, the effects studied in this work would appear to be general in PMMA and to be little influenced by the presence of different initiators and plasticiser although the role of the excess monomer cannot be ruled out completely.

The two types of PMMA have been used to increase the scope of the measurements. In P1 type PMMA the presence of plasticiser induces a strong optical absorption cut-off below 290 nm, and measurements of the OD below this wavelength are made impossible because of stray light effects arising in the spectrophotometer. On the other hand, P1 type PMMA gives a very intense photoluminescence emission. In contrast, P2 type PMMA exhibits an optical cut-off at 250 nm, and consequently the OD spectrum can be studied over a broader wavelength range. The photoluminescent emission of P2 is very poor compared with that of P1 although the emission spectra are similar. This implies that either a very small contamination of plasticiser is present in P2 type PMMA, or that the plasticiser is acting as a form of energy transfer system and as the PL spectrum has been found to be multi-component and is similar to that published by Dészi et al. (1966), the latter explanation is to be preferred.

#### 2.4 Apparatus

#### 2.4.1 Spectrophotometers

The Zeiss PMQ II is a single beam spectrophotometer which is ideal for accurate measurements of OD change at a preselected wavelength. The wavelength region covered by a deuterium lamp and a tungsten lamp is 185 to 2500 nm. The detectors are a photomultiplier tube up to 600 nm and a PbS photocell from 600 to 2500 nm. In the wavelength range used for PMMA (250 to 500 nm), an air path is used to set 100 % transmission and the OD of the samples are measured before and after irradiation.

The Unicam SP 700 A is a double beam ratio recording spectrophotometer which is especially useful for the measurement of OD spectra. An unirradiated sample is used as control and an irradiated sample is compared with the control as the wavelength is automatically scanned through the desired range. The instrument uses a deuterium lamp and a tungsten lamp to cover the range 187-3570 nm. Two different monochromators are used: a prism from 187 to 2500 nm and a grating from 2500 to 3570 nm. Two different detectors are also used: a photomultiplier tube from 187 to 700 nm and a PbS photocell from 700 nm to 3570 nm.

#### 2.4.2 The photoluminescent emission spectrometer

This apparatus has been constructed to measure the spectrum of light emitted by samples following irradiation, either in the form of thermoluminescence or photoluminescence. The apparatus is based on a design by Harris & Jackson (1970) and makes use of a Grubb-Parsons monochromator which has a lithrow system of prism and mirrors so that the spectrum can be scanned by a rotary movement of the mirror. A synchronous motor drives a specially formed cam and a cam follower connected to the axis of the mirror gives the desired rotary motion of the mirror. The cam form ensures that the mirror moves so that the rate of change of wavelength is constant in time, that a spectrum range from 250 to 700 nm is scanned in 0.75 sec, and that a short flyback of 0.25 sec occurs. The spectrometer has been used with a relatively large slit width to improve the detection of the low intensity emitted light and this has resulted in a band width which varied from 30 nm at 300 nm to 100 nm at 600 nm. The spectrally analysed light falls on the photocathode of a wide spectral range photomultiplier (EMI 9698 Q B, quartz

window S 20 cathode). The signal from the photomultiplier is converted from analogue to digital form and the pulses are fed into a multichannel analyser used in the time mode and driven by a frequency generator so that the spectrum range falls over a suitable number of channels. The start of the channel scan is synchronised to that of the spectrum scan, so that each channel represents a certain wavelength. The continued rotation of the cam means that the spectrum is scanned repeatedly, once in every second.



Fig. 3 Schematic diagram of the photoluminescent emission spectrometer.

The system is shown in Fig. 3 set up for the analysis of a photoluminescence emission spectrum when a high pressure mercury lamp or a Xenon lamp is followed by a Zeiss PMQ II monochromator to select the stimulating light. Fig. 4 shows the linearity of the spectrum analysing system, giving a plot of channel number versus the wavelength.

#### 2.4.3 The electron spin resonance spectrometer

The electron spin resonance spectra were obtained at the Radiobiophysics Department of Utrecht University in co-operation with Dr. J.J. ten Bosch. An X-band (9500 MHz) spectrometer was used in which the magnetic field was modulated with 100 KHz with a peak to peak amplitude of not more than 2 x  $10^{-4}$  T (2 gauss). The power level applied to the Varian 4531 cavity was less than 15  $\mu$ W. A synthetic ruby served as an internal standard. This spectrometer has been completely described by ten Bosch (1967). Following a discussion of the various sources of error associated with the measurement of spin concentrations, ten Bosch was not able to give an estimation of the

Wavelength (nm)



overall error. He concluded that comparative measurements on the same material in the same spectrometer could be expected to have an error of 5 % but an absolute determination of the concentration of spins would involve an error of more than 10 %.

#### 2.4.4 The variable temperature unit

This simple unit was constructed to enable PMMA samples to be irradiated at temperatures between  $-196^{\circ}C$  and  $20^{\circ}C$ . The unit consists of two styrofoam boxes, one inside the other, the samples of PMMA being placed on a styrofoam bridge in the inner box. A thermo-couple was mounted in one sample of PMMA and used to check the temperature. A pipe was connected from a closed dewar to the outside box and a nitrogen gas bottle was connected to the closed dewar so that either liquid nitrogen could be forced into the outer box from the dewar, or cold nitrogen gas, bubbled through the liquid nitrogen in the dewar, could be blown into the outer box. An opening was made in the inner box so that the cold gas could also pass over the samples of PMMA, but a baffle was used to prevent the samples from being splashed by the liquid nitrogen.

The unit was used in two ways. Temperatures between  $-196^{\circ}C$  and  $-130^{\circ}C$  were achieved by pouring liquid nitrogen into the inner box to just under

the level of the samples; the box was closed and liquid nitrogen was poured over the lid into the outer box. This box was also closed, and the liquid nitrogen was forced from the dewar into the outer box until the samples reached  $-196^{\circ}$ C. This temperature was maintained by continuing the flow of liquid nitrogen. The temperatures of  $-165^{\circ}$ C and  $-140^{\circ}$ C were achieved by reducing the flow of liquid nitrogen so that the liquid nitrogen in the inner box evaporated and the inner box began to warm. This warming occurred at a slow rate because the outer box still contained liquid nitrogen and the warming rate was controlled by the flow of liquid nitrogen to the outer box. The warming rate was slow enough for the irradiation to be made over a temperature change of  $5^{\circ}$ C at  $-165^{\circ}$ C in a period of 1.25 minutes.

Temperatures between  $-130^{\circ}$ C and  $0^{\circ}$ C were achieved in the following way: the inner box was closed and liquid nitrogen was poured over the lid and into the outer box. This box was also closed and the samples were cooled to below  $-130^{\circ}$ C. The nitrogen gas bottle was connected to the dewar so that instead of applying a pressure to the dewar and forcing liquid nitrogen out, the gas was bubbled through the liquid nitrogen in the dewar and blown into the outer and inner boxes. As long as liquid nitrogen remained in the outside box, the inner box remained at a more or less constant temperature and the samples could be warmed by blowing the cooled gas through the boxes. In this way the temperature of the samples could be controlled accurately enough to allow an irradiation to be made over 1.25 minutes so that the temperature of the samples remained constant within 3-4°C. The temperature homogenity through the samples was better than 3°C.

## **3** Preliminary measurements

It is expedient to consider the basic measurements made on the P1 and P2 types of PNMA and to establish certain important similarities in the radiation response of the two types before discussing various special experiments in detail.

3.1 The optical density spectrum

The OD spectra of P1 and P2 samples of PMMA irradiated and measured at room temperature are shown in Fig. 5. The spectra are alike in the wavelength region where overlap occurs; the spectrum of P1 exhibits a peak at

Optical density



Fig. 5 The spectrum of the induced optical density change in 2 mm thick Pl and P2 samples irradiated at  $20^{\circ}$ C to approximately 1 Mrad.

292 nm which is artificial and may be attributed to stray light conditions in the spectrophotometer. At this wavelength the OD of the unirradiated P1 sample is 0.94. In P2 the induced OD spectrum extends down to 250 nm and exhibits a peak at 262 nm. At this wavelength the OD of the unirradiated P2 sample is 0.97; this peak is also considered to be unreal. In all spectra obtained using P2 samples the results below 260 nm are considered to be open to doubt because the onset of stray light conditions will restrict their validity.

Fig. 6 shows the spectrum of P1 and P2 PMMA samples immediately following a dose of electrons delivered at a high dose rate ( $3 \times 10^6$  rad/s), and 1 hr after the end of the irradiation. The absorption at 800 nm plus one at 600 nm caused by the dibutyl phthalate plasticiser is clearly demonstrated, together with the fact that after 2 hrs this absorption will no longer be of importance and will not affect measurements made on the samples in the wavelength region between 250 and 450 nm.

The radiation induced OD spectra presented in Fig. 5 can be compared



Fig. 6 The optical density spectrum of 2 mm thick Pl and P2 samples after irradiation to 3.5 Mrad at 3 x  $10^6$  rad/s. 1) Pl - 2 min after irradiation. 2) Pl - 7 min after irradiation. 3) Pl - 1 h after irradiation. 4) P2 - 9 min after irradiation. with OD spectra published in the literature for other types of PMMA (Boag et al., 1958; Orton, 1966; Muller et al., 1966; Berry & Marshall, 1969). In measurements above 292 nm the agreement is good in all cases, below this wavelength considerable differences occur. Orton and Muller et al. show spectra exhibiting peaks at many different wavelengths, but as they have not considered the effect of stray light on their spectra, it is difficult to know if the peaks which they find are real or experimental artefacts. One spectrum published by Orton, where stray light conditions did not exist, shows a smooth spectrum down to 260 nm which is more in overall agreement with the measurements presented here. Boag et al. (1958) and Berry & Marshall (1969) have not published spectra below 290 nm.

If irradiated PMMA samples are allowed to stand in air, a part of the induced OD fades slowly following the diffusion of oxygen (Fowler & Day, 1955; Boag et al., 1958; Orton, 1966) and after some weeks, and on complete oxygen diffusion, an oxygen stable OD remains (Chadwick, 1969). The spectrum of this stable OD is shown in Fig. 7 for P2 PMMA; it is a smooth spectrum increasing rapidly from 280 nm to 260 nm, has a long tail up to 350 nm, but

**Optical density** 



Fig. 7 The optical density spectrum of a P2 sample irradiated to 800 krad and stabilized in oxygen.

it exhibits no peak.

The OD spectrum of a P2 sample irradiated with electrons at  $-160^{\circ}$ C is shown in Fig. 8. The spectrum is basically similar to that shown in Fig. 5, except that a broad peak occurs at 270-280 nm. Comparing Fig. 5 and Fig. 8, it would appear that the difference between the spectra would result in a spectrum not unlike that shown in Fig. 7, which would mean that the stable OD component is not formed on irradiation at  $-160^{\circ}$ C. This surmise is borne out in the photoluminescent measurements (see 3.2).

#### Optical density



Fig. 8 The optical density spectrum of a P2 sample irradiated at  $-160^{\circ}$ C to 1.2 Mrad.

#### 3.2 The photoluminescent emission spectrum

The PL emission spectrum of P1 and P2 PMMA samples irradiated and measured at room temperature are shown in Fig. 9. The emission was stimulated using monochromatic light of 313 nm. The spectra are similar in that both appear to be two component, one component emitting in the region 400-450 nm, the other in the region of 550 nm. The striking difference between the two samples lies in the intensity of the light emission; the OD of the two samples of PMMA is very similar at 313 nm after the same dose of radiation,





but under the same conditions the emission from the P1 sample is much greater than that from the P2 sample. This difference must be ascribed to the presence of the plasticiser dibutyl phthalate in the P1 sample. In this respect it is interesting to note that the emission spectra published by Dészi et al. (1966) are also two component and also show an emission in the regions 400-450 nm and 550 nm. The samples used by Dészi et al. were manufactured in Eastern Europe and, although no contaminants are specified, the similarity in the different spectra suggests that the emission is basic to the PMMA and is not directly associated with the plasticiser.

Fig. 10a shows the PL emission spectrum from a P1 sample which was stored in air until complete oxygen diffusion had taken place and only the stable OD remained, the emission is at 440 nm. The PL emission spectrum of a P1 sample irradiated with electrons at  $-160^{\circ}$ C is shown in Fig. 10b and reveals that the component emitting at 440 nm is almost completely absent and that only the emission at 580 nm is of importance. This measurement is in agreement with the OD spectrum measurements and demonstrates that the oxygen stable species is not formed when PNMA samples are irradiated at low

PL emission (arb, units)

PL emission (arb. units)



temperature. When a sample of room temperature irradiated PMMA is subjected to a heat treatment of  $130^{\circ}$ C for 5 min, the PL emission which remains, shown in Fig. 10c, is the same as that which has been associated with the oxygen stable species.

#### 3.3 The electron spin resonance spectrum

As has been previously stated, gamma irradiation of PMMA leads to a nine line ESR spectrum. Fig. 11 shows the ESR spectra found in samples of P1 and P2 after gamma and electron irradiation at room temperature, electron irradiation at  $-160^{\circ}$ C, and fast neutron irradiation at room temperature. In every case the typical nine line spectrum has been found. Following complete



Fig. 11 The electron spin resonance spectrum in Pl and P2 samples.

a) P1, irradiated at  $20^{\circ}$ C to I Mrad with I.5 MeV X rays. b) P2, irradiated at  $20^{\circ}$ C to I Mrad with I.5 MeV X rays. c) P2, irradiated at  $-160^{\circ}$ C to I Mrad with I.5 MeV electrons. d) P1, irradiated at  $20^{\circ}$ C to

0.8 Mrad with fast neutrons. e) P2, irradiated at  $20^{\circ}$ C to 0.8 Mrad with fast neutrons.

oxygen diffusion or heat treatment at  $130^{\circ}$ C for 5 min no ESR signal was observed.

# 4 An interpretation of the optical density - dose relationship in irradiated clear polymethyl methacrylate

### 4.1 Introduction

Radiation induces an absorption band in clear polymethyl methacrylate (PMMA) which extends from the near UV to 400 nm. As a result of this absorption band, the PMMA becomes yellow-brown and, as the optical density (OD) associated with the colouring is singularly related to radiation dose and is relatively stable, the system has been proposed and used for radiation dosimetry (Fowler & Day, 1955; Boag et al., 1958).

The use of the induced OD change in clear PMMA for radiation dosimetry has been the subject of several publications. Some of these publications have been solely concerned with the practical aspects involved in the calibration and use of a PMMA dosimetry system (Davidson & Sutton, 1964; Muller et al., 1966; Chadwick, 1969), whilst one or two publications have described more detailed investigations of the various parameters influencing the radiation induced effect in the PMMA (Boag et al., 1958; Orton, 1966). None of these publications have discussed the processes occurring in the irradiated PMMA which lead to, or cause the OD change. It is the purpose of this chapter to propose a model of the radiation processes which leads to an analysis of the OD-dose relationship.

## 4.2 Results

The OD-dose relationship of normal PMMA exhibits a non-linear, reproducible form at all the wavelengths used (Fig. 12). The curve passes through the origin, is roughly proportional to the square of the dose up to 150 krad, is linear from 150 krad to 500 krad, above which it becomes sublinear.

The OD-dose relationship of pretreated PMMA is linear from the origin to approximately 500 krad, above which it becomes sublinear (Fig. 13).

A small difference in sensitivity between P1 and P2 has been found at low doses but this is not regarded as significant as different plates of P1

Optical density



20 Fig. !2 The OD-dose relationship of normal PMMA (2 mm) at Dose (Mrad) different wavelengths.

Optical density



Fig. 13 The OD-dose relationship of pretreated PMMA (2 mm) at different wavelengths. give also slightly different calibration curves.

In an experiment using P1 where the dose range was extended to 10 Mrad no saturation of the dose curve was found although the curve became increasingly sublinear.

If the irradiated PMMA is stored in the dark in oxygen or air after irradiation the OD fades exponentially, due to interaction with the diffusing oxygen, but on complete diffusion a very stable OD remains (Fig. 14). This stable OD also exhibits a smooth relationship with the radiation dose (Fig. 15). The curve passes through the origin and becomes sublinear although this occurs at a slower rate than the total OD-dose curve.

Optical density



Fig. 14 The fading of the OD in irradiated PMMA (2 mm) on 0, diffusion.

Optical density



Fig. 15 The OD-dose relationship of the oxygen stable OD component at different wavelengths.

4.3 Analysis of results

The experimental results can be explained on the basis that the total OD is made up of two components, an oxygen unstable component and an oxygen stable component. It has been found that the oxygen unstable component is temperature unstable whilst the oxygen stable component is also temperature stable.

In order to continue the analysis further it is necessary to consider each component separately and to propose a model which describes the processes which may occur.

### 4.3.1 The unstable OD component

The model which is proposed to describe the unstable OD component is based on the following processes:

- radiation causes scissions in the molecular chain,
- a proportion of the main chain scissions leads to radical formation,
- the radicals have a probability of being annihilated by the radiation,
- the OD is proportional to the number of radicals remaining at the end of irradiation.

This model is similar to that proposed by Müller (1966) and Horan & Snipes (1967) for the production and destruction of radicals and which is used to describe the relationship between radical concentration and dose. The assumption that main chain scission precedes radical formation in PMMA is reasonable in view of the evidence arising from ESR measurements presented by Kourim & Vacek (1965) and by Bullock & Sutcliffe (1964) on the possible nature of the formed radicals.

It follows then that if:

- $\rm N_{_{O}}$  is the original number of targets for main chain scission per  $\rm gm$
- N is the number of targets per gm at dose D
- σ is the probability per target per unit dose for main chain scission
- is the probability per radical per unit dose that a formed radical is destroyed by radiation
- R is the number of radicals per gm at dose D
- p is the proportion of main chain scissions which forms radicals,

$$\frac{dN}{dD} = -\sigma N$$
 and  $N = N_o e^{-\sigma D}$ 

and

which leads to  $R = \frac{p\sigma N_o}{\phi - \sigma} (e^{-\sigma D} - e^{-\phi D})$ 

 $\frac{dR}{dD} = p\sigma N - \phi R$ 

and

d  $OD_{\lambda} = k_{\lambda} \frac{p\sigma N_{o}}{\phi - \sigma} (e^{-\sigma D} - e^{-\phi D})$  (3)

where  $k_\lambda$  is related to the extinction coefficient of the radical and the geometry of the sample at the wavelength  $\lambda$  at room temperature.

An estimate of the relative magnitudes of  $\sigma$  and  $\phi$  is possible by reference to literature. Wall & Brown (1957) have published figures showing a linear relationship between number of scissions and dose up to 16 Mrads with no indication of saturation. These results indicate that  $\sigma$  is relatively small ( $\sigma$ D << 1 in range D = 0-10 Mrads). On the other hand Horan & Snipes (1967, 1969) have recently published results showing that the annihilation

of radicals in organic compounds is a very efficient first order process. These results indicate that  $\phi$  is relatively large and will play a dominant role in the above equation. Thus equation (3) may be approximated to

$$OD_{\lambda} = k_{\lambda} \frac{p\sigma N_o}{\phi} (1 - e^{-\phi D}).$$

In practice the most reproducible results in the OD measurements have been found at 314 nm (Chadwick, 1969) and a best fit of an equation of the form

$$OD_{314} = K_{314} (1 - e^{-\phi D})$$

has been made to the experimental data for the 2 mm thick pretreated PMMA, to which these equations apply, using the method of least mean squares (Fig. 16). The experimental data were obtained by subtracting the stable OD from the initial total OD. The best fit was obtained with values of  $K_{314} = 1.228$  and  $\phi = 0.401$  per Mrad.

#### 4.3.2 The stable OD component

The model which is proposed to describe the stable OD component is Optical density  $$\lambda$\,314\ nm$$ 



Fig. 16 Fit of model equations to experimental results for OD-dose relationship in pretreated PMMA; unstable OD = 1.228 (1 -  $e^{-0.401}$  D), Dose (Mrad) stable OD = 1.96 (1 -  $e^{-0.045}$  D). based on the following processes:

- the radiation causes a side chain break which leads to a fragment having an optical absorption between 260-330 nm,
- the fragments have a probability of being involved in a radiation induced interaction such that they no longer exhibit an optical absorption between 260-330 nm,
- the OD is proportional to the number of fragments remaining at the end of irradiation.

Using similar arguments as have been used in the case of the unstable component the stable OD-dose relationship may be approximated by an equation of the form

$$OD_{\lambda}^{S} = k_{\lambda}^{S} \frac{\eta L_{o}}{\delta} \qquad (1 - e^{-\delta D}) = K_{\lambda}^{S} (1 - e^{-\delta D})$$

where L is the original number of targets for fragmentation per g

- n is the probability per target per unit dose for fragmentation
- δ is the probability per fragment per unit dose that a fragment is destroyed by radiation
- $k_{\lambda}^{S}$  is related to the extinction coefficient of the fragment and the geometry of the sample at  $\lambda$  at room temperature.

A fit of an equation of this form has been made to the experimental data at  $\lambda$  = 314 nm using the method of least mean squares and the best fit was obtained with values of  $K_{314}^S$  = 1.96 and  $\delta$  = 0.045 per Mrad (Fig. 16).

It is further assumed that molecular oxygen does not interfere in this process.

4.3.3 The effect of molecular oxygen on the unstable OD component

In the case of the normal PMMA, when the molecular oxygen present in the polymer matrix modifies the OD-dose relationship, the model proposes that the oxygen attacks the radicals formed to produce peroxy radicals which do not contribute to the OD. This causes a modification of the differential equations so that

$$\frac{dN}{dD} = -\sigma N \quad \text{and} \quad N = N_o e^{-\sigma D},$$
$$\frac{dR}{dD} = p\sigma N - \phi R - \beta RM, \text{ and} \quad \frac{dM}{dD} = -\beta RM,$$

where M is the number of oxygen molecules remaining after a dose D, and  $\beta$  is the probability that a radical and an oxygen molecule will meet and react per unit dose.

These equations cannot be solved explicitly but an approach to the solution may be made by assuming that the unstable OD is zero up to the moment when the molecular oxygen is burnt up. A good fit of the experimental results is obtained if

> $OD_{314} = 0$  for D < 0.09 Mrad and .  $OD_{314} = 1.228 (1 - e^{-0.401 (D-0.09)})$  for D > 0.09 Mrad (Fig. 17),

i.e. the unstable component originates at 90 krad.

Whilst the threshold of this effect will not, in practice, be as sharp as is assumed the approximation gives a good indication of what may be expected from the differential equations and also indicates that the oxygen will be burnt up at a dose of approximately 100 krad which is similar to the value of 150 krad found in polyethylene (Charlesby & Partridge, 1963).



Fig. 17 Fit of modified model equations to experimental results for OD-dose relationship in normal PNMA; OD =  $1.228 (1 - e^{-0.401(D-0.09)}) +$  $1.96 (1 - e^{-0.045 D}).$ 

#### 4.4 Discussion

#### 4.4.1 The model proposed for the unstable OD component

The model of radical production and annihilation appears to be reasonable and there is evidence in literature to support it. Rotblat & Simmons (1963), Müller (1963,1964), Kohnlein & Müller (1964), Müller & Kohnlein (1964), Müller et al. (1964), and Casteleijn et al. (1964) have shown that the free radical concentration is related to dose by an equation of the form

$$\frac{C}{C_{\infty}} = (1 - e^{-D/D} 37)$$

where  $C_{\infty}$  is the concentration of free radicals at saturation and  $D_{37}$  is the dose at which the radical concentration is 63 % of  $C_{\infty}$ .

Following an initial suggestion in 1963 that radical production and stabilization would give such a relationship Müller (1966) later suggested that a dynamic equilibrium between production and destruction would explain the radical saturation. Horan & Snipes (1967,1969) adopted the proposal and demonstrated that the radical destruction by radiation occurs through a very efficient first order process. The coefficients for radical destruction which they have measured for various organic materials are in the order of 0.1 Mrad<sup>-1</sup> which is the same order of magnitude that has been measured here, i.e.  $\phi = 0.4 \text{ Mrad}^{-1}$  for PMMA. In explaining their results Horan & Snipes (1968,1969) prefer an energy transfer process involving charge transfer correlating free radical measurements with those of electrical conduction. This explanation is also appealing in the case of PMMA in view of the rigidity of the material and the radiation induced conduction. If the process of radical destruction occurs through some intermolecular energy transfer process then the preparation, purification and environment of a sample will most probably play an important role in the development of the radical concentration with dose and it is therefore not surprising that the same material from different origins exhibits differing radiation sensitivities.

One other interesting feature of the model presented here is that the complete equation for the radical-dose relationship:

$$R = \frac{p\sigma N_o}{\phi - \sigma} (e^{-\sigma D} - e^{-\phi D})$$

predicts that at high doses, when oD begins to be effective, the radical

concentration will decrease from the saturation concentration. This phenomenon has been found by Rotblat & Simmons (1963) in polycrystalline glycine above 40 Mrads and by Schoffa (1966) in amino acids above 50 Mrad. De Bie (1968) has also found a saturation and decrease in radical concentration in glycine at 20 Mrad and has shown that the chemical products increase steadily to beyond 200 Mrad. This is evidence in favour of the continued production of radicals beyond the saturation dose. It is difficult to predict the dose at which this effect will occur in PMMA but it will most certainly be above 20 Mrads as the relationship between scissions and dose is strictly linear below 20 Mrads.

The model of radical production and annihilation which has been used to explain the unstable OD component has been selected after consideration of two other possible models which give similar OD-dose equations.

One model which has been considered and discarded is the target model for radical production which renders the equation

 $OD = K (1 - e^{-\sigma}R^{D})$ 

but raises the problem that it only predicts a saturation of the OD and radical concentration. In addition with a saturation dose of 12 Mrads and a G value of 2 (Abraham et al., 1958) the model predicts one target for radical production per 400 monomer units which appears to be small as a second break in a chain of 400 monomer units may also be expected to give rise to radical formation.

A second model which has also been considered is that of electron trapping. Fowler (1956) has explained the radiation induced conduction in PMMA and other polymers using the electron trapping processes and the photoelectric theory with considerable success. In addition Barnes et al. (1969) have found a conduction pulse in irradiated PMMA on warming and have discussed in detail the nature of electron traps in different polymers. It is also relevant to mention that several of the OD and photoluminescent phenomena in PMMA investigated by the author may be reasonably explained on the basis of electron trapping, except possibly the fact that a small change occurs in the radiation induced OD spectrum on warming. This is more easily explained on the basis of a change in radical configuration (Symons, 1963) or the conversion of one radical species into another radical species (Bullock & Sutcliffe) than by a change in the electron trap distribution. Although this model cannot be completely excluded it does seem less

plausible and preference has been given to the model of radical production and annihilation.

One further piece of experimental evidence which fits consequentially in the model is that if a PMMA sample irradiated to 2.5 Mrad is allowed to fade in oxygen to a stable OD and is then reirradiated to 500 krad, the increase in OD is in agreement with that calculated for an unirradiated normal sample. This evidence can also be fitted in the electron trapping model when the assumption is made that the oxygen empties the electron trap without interacting with the trap. The model for radical production and annihilation only requires that the diffusing oxygen reacts with the radical to form another species.

#### 4.4.2 The model proposed for the stable OD component

There is no direct evidence either for or against the proposal of fragmentation but the fact that the two components differ has been shown in photoluminescence studies which reveal two peaks in the emission spectrum (Fig. 18). The peak at 450 nm correlates with the stable OD component and the peak at 560 nm correlates with the unstable OD component. It has also been shown that prolonged heating of unirradiated PMMA at  $100^{\circ}$ C in air or vacuum causes the development of an OD which gives the same photoluminescent emission spectrum as the stable OD component in irradiated PMMA, and this fact suggests that a dissociation phenomenon is involved.

The possibility that the destruction of a radical might lead to the stable OD has also been considered, especially in view of the fact that the OD spectra of the two components are similar, but has been discarded on the grounds that the relation with dose would be initially quadratic and neither OD nor photoluminescent measurements have given this relationship. It is also possible that the stable OD-dose relationship may be described by a target theory of fragmentation. This, however, would imply that the probability for fragmentation is an order of magnitude larger than the probability for main chain scission, i.e. n would be 0.045 Mrad<sup>-1</sup> and  $\sigma << \phi = 0.401 \text{ Mrad}^{-1}$  so that n >  $\sigma$  and this seems unlikely. What appears to be more likely is that the probabilities for fragmentation and main chain scission are of the same order and that the probability for the annihilation of a radical is some 10 times larger than that for annihilation of a fragment.

It is concluded that the OD-dose relationship in PMMA may be reasonably

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These values of  $\phi$ ,  $\sigma$  and  $N_0 \cdot p.\sigma/\phi-\sigma$  indicate that the value of p decreases by a factor of the order of 3 from He<sup>4</sup> ions to Ar<sup>40</sup> ions. The change in p might be explained on the basis of more recombination effects occurring with the more densely ionizing radiation. In this respect the results must be treated with some caution as the hypothesis applies to one radical type only and Henriksen's results show that the ESR spectrum changes at high doses, although the change is not very large in the case of A<sup>40</sup> ions.

5.4.2 The stable OD component

In this case the difference in results between the neutron and gamma







Fig. 22 Comparison of the OD-dose relationship in Pl following gamma and fast neutron irradiation.

and, assuming that  $K_{\lambda}$  and  $N_{O}$  remain constant, the change in G value of yield is associated with a change in either  $\sigma$ , the probability per unit dose that a main chain is broken, or p, the probability that a main chain break forms a radical. In view of the results quoted by Lavrentovich et al. (1970), where the degradation of PMMA has been found to decrease with increasing average LET of the radiation, the value of  $\sigma$  is certainly dependent on the LET of the radiation and consequently affects the G value. This does not ex-

irradiated PMMA is not very great, either in production or in destruction, and the development of the stable component appears to depend on the energy absorbed from the radiation rather than on the LET of the radiation. This might be explained on the basis that the process is a dissociation process and that the product is very stable, and thus the chance for recombination is much lower than in the case of the unstable OD component.

#### 5.4.3 The comparison of P1 and P2 type of PMMA

In comparing the results for P1 and P2 types of PMMA it can be seen that the plasticiser plays little role in the development of the OD but that the breakdown of the unstable OD component is more efficient in the presence of the plasticiser. This effect could be explained on the basis of some form of process involving the plasticiser.

#### 5.4.4 Conclusion

It is concluded that following fast neutron irradiation of PMMA the ODdose relationship can be represented by the sum of a radical production and annihilation process, and a fragment production and annihilation process. The radical production and the coefficient for radical annihilation are lower than in the case of gamma irradiation whilst the production and destruction of the fragments is little influenced by the two different types

of radiation.

The use of clear PMMA as a radiation dosimeter in a fast neutron field is obviously limited. The development of the OD has been related to fast neutron dose but the analysis has indicated that the response will be dependent upon LET of the radiation and hence to some extent on the fast neutron spectrum. A second parameter which will play a role is the gamma contamination of the fast neutron beam. In the Barn reactor this amounts to only 5-10 % of the neutron dose, in other facilities when the gamma contamination reaches important proportions (~ 25 %) a significant part of the OD will be caused by this, more effective, low LET radiation. It is concluded therefore that clear PMMA is not a suitable dosimeter for fast neutrons although it may be calibrated for use as a dose monitor in a special facility.

## 6 The correlation between the unstable optical density component and the free radical species in irradiated polymethyl methacrylate

#### 6.1 Introduction

In the previous two chapters a hypothesis has been developed to explain the dependence of the unstable component of the OD with radiation dose on the basic assumption that the unstable OD is caused by the radical species formed in PMMA on irradiation and can be identified by the nine line ESR spectrum. It is necessary to justify this basic assumption.

The correlation between the optical density and the radicals induced in irradiated PMMA was studied by Verhelst (1970). He considered the correlation between the total optical density and the radical concentration using the dose effect relationships and the decay of radicals on heating, and he concluded that the correlation was not good.

The following discussion and evaluation of experimental results is intended to show that a correlation does exist between the unstable OD and the radical concentration, and to show that they are one and the same thing.

6.2 The equivalent behaviour of the unstable OD and the radicals

The free radical nine line spectrum and the unstable OD in PMMA react to certain physical phenomena in a similar way, and whilst these reactions do not prove the correspondence between the two parameters, they are evidence in favour of it.

6.2.1 The effect of oxygen in the PMMA matrix on the dose response

It has been shown in Chapter 4 that irradiation of untreated PMMA, when oxygen is present in the plastic matrix, leads to an OD-dose response which is approximately parabolic over the first 150-200 krad due to the fact that the unstable OD component is not formed until the oxygen in the PMMA matrix has been burnt up by the radiation. The radiation dose for 'burn up' has been estimated to be 90 krad. A similar curve has also been found by

Verhelst for the radical concentration versus dose, and the 'burn up' dose can be estimated by extrapolation of his curve to be between 100 and 125 krad. Verhelst also found peroxyradicals at these low doses, but Lefebvre (1968) has investigated the peroxyradicals formed in PMMA in more detail and found that the number of these radicals increased to a certain level and dose, above which the radical concentration decreased. Lefebvre also found that the typical nine line radical spectrum did not start to develop until the peroxy radical peak had been reached. The 'burn up' dose estimated from the work of Lefebvre is approximately 100 krad. Optical density



Fig. 24 The effect of storage in the dark in vacuum and nitrogen on the OD in Pl.

#### 6.2.2 The effect of oxygen diffusion in irradiated PMMA

It has been shown in Chapter 4 that, if irradiated PMMA is stored in air or oxygen in the dark, the diffusion of gas molecules into the PMMA causes the unstable OD component to fade, and on complete gas diffusion no unstable OD remains. This effect of gas diffusion on the OD has also been reported in the literature (Fowler & Day, 1955; Boag et al., 1958; Orton, 1966; Chadwick & Leenhouts, 1970).

If the irradiated PMMA is stored in nitrogen or vacuum after irradiation, this fading of the OD does not occur (Fig. 24). The induced fading has been ascribed to oxygen reactions with the centres which cause the unstable optical density. An experiment has been carried out to study the fading of the OD and radical concentration in P1 and P2 samples on oxygen diffusion. The results of this experiment are given in Fig. 25 and show that the unstable OD and radical concentration fade at the same rate, though this rate is different in P1 and P2.

6.2.3 The effect of temperature on irradiated PMMA

The studies of the effect of heating on the free radical spectrum in



Fig. 25 Comparison of the fading of the unstable OD and radical concentration in PI and P2 on oxygen diffusion.

irradiated PMMA have been the main cause for the controversy which exists in the identification of the nine line ESR spectrum (Campbell & Looney, 1962; Symons, 1963; Bullock & Sutcliffe, 1964; Michel et al., 1967). Two temperature regions seem to be important in this respect, between  $50-80^{\circ}$ C, and above  $80^{\circ}$ C.

In the region between 50 and  $80^{\circ}$ C the shape of the nine line spectrum has been found to change (Bresler et al., 1959; Campbell & Looney, 1962; Bullock & Sutcliffe, 1964; Michel et al., 1967), the centre line of the nine indicating a fading of the signal, the change in shape indicating the possible co-existence of two radicals of different temperature sensitivity. Following extended heating at  $80^{\circ}$ C, Michel et al. (1967) have found that a small broad singlet ESR spectrum remains. Verhelst (1970) has also mentioned that the ESR spectral shape changes in time on heating at different temperatures. Symons (1963) has studied the effect of  $110^{\circ}$ C on the ESR spectrum and found no change in the spectral shape during the fading process.

On treatment at  $55^{\circ}C$  the OD spectrum in irradiated PMMA has been found to change. Above 320 nm the OD decreases, but between 280 nm and 320 nm the OD increases; the change is not dramatic but reproducible and obvious (Fig. 26). At temperatures above  $70^{\circ}C$  the complete spectrum fades. It has been found that following extended fading at these temperatures, higher levels of the stable OD component remain than would be expected after oxygen diffusion. This indicates that the process which causes the change in OD spectrum may also result in the development of the stable OD component. It will be seen in the following section, and also in Chapter 7, that the exposure of irradiated PMMA to light causes the development of the OD in the wavelength region 280-330 nm and that this is associated with a change in the ESR spectrum.

A five minute treatment of irradiated PMMA at 150<sup>o</sup>C under vacuum fades the unstable OD completely, and only the stable OD component remains at the level normally found after oxygen diffusion. No ESR signal has been found in a sample treated in this way.

#### 6.2.4 The effect of light exposure on irradiated PMMA

When irradiated PMMA is exposed to light in the near UV region, the OD spectrum changes (Whittaker and Lowe, 1967). Under 340-390 nm light a peak develops in the 300 nm region of the OD spectrum and the nine line ESR spectrum undergoes an obvious change, the nine line spectrum fades and a second



Fig. 26 The change in OD spectrum in a P2 sample on heating. 1) freshly irradiated, 2) after  $55^{\circ}$ C for 30 min.

spectrum appears. The development of the OD peak correlates with the fading of the central line of the ESR spectrum and, as the total number of spins remains the same, it also correlates with the development of the second ESR spectrum.

This effect will be dealt with in greater detail in Chapter 7.

# 6.3 The correlation between the ESR-dose relationship and the OD-dose relationship after gamma irradiation

Verhelst has made measurements of the free radical spin concentration versus dose in pretreated P1 type PMMA and a correlation has been made between his measurements and unstable OD component measurements at 314 nm as shown in Fig. 16 of Chapter 4. The radiation dose has been used as the common parameter and the free radical spin concentration is shown plotted against the corresponding OD value in Fig. 27. The best straight line



calculated using the method of least mean squares has been drawn through the points, the correlation coefficient r is +0.995, and the regression line is represented by the equation

$$R = (4.88 \text{ OD}_{314} - 0.18) \ 10^{18} \text{ spins/g}.$$

where R is the free radical concentration.

In view of the fact that these results arise from two different experiments, one using 50 kV X-rays, the other 137Cs and 60Co gamma rays, the correlation between the two parameters is excellent.

# 6.4 The correlation between the ESR-dose relationship and the OD-dose relationship following fast neutron irradiation

The fast neutron irradiation of PMMA has been reported in Chapter 5 and in the same experiment samples of P1 and P2 were irradiated for radical determinations. The ESR measurements have been made at Utrecht University and were carried out by Dr. J.J. ten Bosch. The ESR spectrum found following fast neutron irradiation is the same nine line spectrum that is found following gamma irradiation.

The peak to peak height of the central line in the ESR spectrum has been plotted against the unstable OD component at 314 nm using the fast neutron dose as the common factor (Fig. 28). The linear correlation between the two parameters has been calculated for P1 and P2 separately.

P1 type PMMA:  $R = 497.3 \text{ OD}_{314} + 16.6$  (arbitrary units) r = +0.93P2 type PMMA: R = 608 OD + 6.4 (arbitrary units) r = +0.96

Although the correlation coefficients are not as high as in the case of the gamma irradiation the results are satisfactory, especially in view of the long duration of the experiment and the different fading characteristics of the ESR and OD samples. The fact that the P2 correlation is better than the P1 correlation indicates that fading may well be the cause of the poorer correlation, as oxygen has been shown to diffuse more rapidly into P1 than into P2.

6.5 The correlation between radical concentration and OD following electron irradiation at different temperatures

Samples of P1 and P2 type PMMA were irradiated at different tempera-



Fig. 28 Correlation between radical concentration and unstable OD component at different doses of fast neutron radiation. a) in Pl, R = 497.3  $OD_{314}$  + 16.6; b) in P2, R = 608  $OD_{314}$  + 6.4.

tures, in the styrofoam box system, described previously, with 1.5 MeV electrons from the Van de Graaff generator. The dose rate delivered to the samples was kept constant, using the electron copter apparatus as control, and the exposure time was set at 1.25 min using an electronically controlled pneumatic shutter. The mean reading of the electron copter was adjusted by varying the beam current of the generator to give 15.2 ± 2.5 % mV and the dose was 1.2 Mrad. The samples were irradiated in the dark at temperatures of -190°C, -165°C, -140°C, -100°C, -50°C and 20°C. After irradiation the samples were allowed to warm up to approximately -80°C and were then transferred in a darkened room to a closed box where they warmed quickly to room temperature also in the dark. OD measurements had been made at 314 nm prior to irradiation and the second OD measurements were made two hours after irradiation to allow the green colour in the P1 samples to fade. The OD spectra of the P2 samples were also measured and were found to be similar to those found on room temperature irradiation. The OD samples were placed in  $O_2$  in the dark and, following complete oxygen diffusion, the stable OD was measured. The ESR samples were stored overnight in the dark under vacuum and were measured the following day by Dr. J.J. ten Bosch at Utrecht University. All ESR samples exhibited the familiar nine line spectrum.

The unstable OD and the radical concentration were found to be dependent





#### Radical concentration





on the temperature during irradiation, Fig. 29 and the values measured have been correlated with each other using irradiation temperature as the common factor. The results are shown in Fig. 30; for P1 the straight line is given by the equation

R = 938.2  $OD_{314}$  - 1.46 (arbitrary units) r = +0.994 for P2 the straight line is given by the equation

 $R = 1308 \text{ OD}_{314} - 4.22$  (arbitrary units) r = +0.990

6.6 Conclusion

In all the aspects considered the radical species and the unstable OD component in the irradiated PMMA react in an equivalent way. In the relationship with gamma dose and dependence on the irradiation temperature the two parameters are extremely well correlated with each other. In the relationship with neutron dose the correlation is good, though not as good as in the other experiments; this has been ascribed to the long duration of the experiment at the different fading in the OD and ESR samples. It is possible to consider the correlation of the two parameters further. It is proposed that the parameters are in fact different measurements of one and the same species. In this case the correlation between the two parameters should be linear and pass through the zero point, and the ratio of the radical concentration to unstable OD should be constant for the different measurements. In all cases the regression lines pass very closely to the origin, but not quite through it, this small difference may be due to an error in the unstable OD which arises from the subtraction of two measurements. It should be noted here that the value of the ratio is not expected to be the same for both types of PMMA.

Thus an attempt has been made to normalise the measurements made by Verhelst (1970) in the radical versus gamma dose relationship and the measurements made in the radical concentration at different irradiation temperatures, and the ratio of the radical concentration (peak-peak, centre line, ESR spectrum) to unstable OD arising from these two experiments has been compared for P1 samples. The fast neutron irradiation experiment has not been considered in this comparison because the ratio is expected a priori to have been affected by the fading effects.

The values of spins/g quoted by Verhelst have been recalculated to peakpeak values for the nine line spectrum using the calibration quoted by Verhelst that each millimetre peak-peak (p-p) was equivalent to  $5.9 \ 10^{13}$ spins/g. These values have been normalised to those of the second experiment using the internal ruby standard in the ESR apparatus. The mean ratio and standard deviation for each experiment have been determined:

Gamma dose relationship: mean  $(p-p)_{OD_{314}} = 75050 \pm 6780$ 

Irradiation temperature dependence: mean  $(p-p)_{OD_{314}} = 58520 \pm 2820$ The mean values are within 25 % of each other which, in view of the errors involved in the different measurements, is a reasonable agreement.

It is concluded that the radical concentration and the unstable OD component are well correlated and that the basic assumption made in Chapter 4 and 5 to explain the OD-dose relationships is justified.

# 7 The photosentive effect in irradiated clear polymethyl methacrylate

#### 7.1 Introduction

Irradiation of clear PMMA produces an optical absorption band in the wavelength range from 250 nm to 400 nm. This radiation induced absorption band is not stable and fades on oxygen diffusion and on heat treatment above  $70^{\circ}$ C. It is also photosensitive, as has been demonstrated by Whittaker & Lowe (1967), and the absorption increases considerably in intensity on exposure of the irradiated PMMA to light in the UV region. On extended exposure to light the absorption band is also bleached (Chadwick, 1969). The practical aspects of this phenomenon in radiation dosimetry have been discussed previously (Chadwick, 1971) but it can also be used to obtain a better insight into the processes which are occurring in the irradiated PMMA on exposure to light.

#### 7.2 Materials and methods

In the region of the cut-off wavelength, stray light conditions begin to affect the OD measurements and consequently the OD spectral measurements on P2 samples are shown with a dotted line between 250-265 nm, indicating that stray light conditions may prevail.

ESR measurements have been made in cooperation with Dr. J.J. ten Bosch of the Radiobiophysics group at Utrecht University, using the apparatus described in section 2.4.3.

The samples of PMMA have been exposed to a TL 'black light' source which emits in the wavelength range 320-390 nm with a peak at 350 nm. The exposures have been made in two stages: first the samples were exposed in vacuo in pyrex glass flasks with an optical cut-off at 340 nm to light in the wavelength region 340-390 nm only. The second exposure was made in air to the complete wavelength range of the 'black light' (320-390 nm). The second exposure was limited to a period over which the diffusion of oxygen into the samples could not be expected to play an important role. Exposures were made

in the centre and 20 cm from a normal two tube TL armature using Philips type TL 40 W/08 tubes.

#### 7.3 Results

On exposure under vacuum to light in the 340-390 nm range, the initial



OD spectrum of the irradiated samples undergoes a drastic change and a new second species is developed which absorbs strongly at 300 nm (Fig. 31). Following each exposure samples were stored in the dark in oxygen until a stable optical density was obtained. Fig. 32 shows that the stable optical density is also developed during this exposure.

Fig. 33 shows the effect of the 340-390 nm light on the ESR spectrum of the P2 samples. This figure illustrates the fading of the initial nine line spectrum and the development of a second ESR spectrum which appears to be a broad singlet. The fading of the nine line spectrum, measured by the fading of the central line, which is least distorted by the new spectrum, has been correlated with the increase in the unstable OD at 314 nm (Fig. 34). In this figure account has been made for the fading of the initial OD spectrum as indicated by the fading of the initial ESR spectrum. If the fading of the initial OD is not considered, the correlation is not as good as that shown in Fig. 34.

Following extended exposure of the samples to the 340-390 nm light, the OD peak height at 300 nm stabilised and the samples were then exposed to the

x 3.3

Fig. 33 The effect of 340-390 nm light on the ESR spectrum of a P2 sample irradiated to 2 Mrad. 1) no exposure, 2) 10 h, 3) 30 h, 4) 40 h, 5) P2 irradiated to 1 Mrad exposure 8 days.

2<sup>nd</sup> Species

optical density 314 nm



Fig. 34 The correlation between the increase in OD at 314 nm and the fading of the original ESR spectrum on exposure to 340-390 nm light.

320-390 nm light, and the action of this light on the second species was studied by both ESR and OD measurements. The change in the OD spectrum on exposure to the 320-390 nm light is shown in Fig. 35: the second species absorbing at 300 nm fades and a third species is formed which absorbs in the region of 270 nm. The OD spectrum of the third species is shown in Fig. 36 and is identical to the stable OD component formed on irradiation. The third species has also been found to be temperature and oxygen stable. The spectrum of the stable OD has been subtracted from the spectra in Fig. 35 after normalisation at 265 nm, the correlation between the decrease in the OD at 305 nm and the increase at 270 nm is shown in Fig. 37. The ESR spectra





(Fig. 38) measured after exposure to the 320-390 nm light, do not indicate the development of any new radical species and so are in agreement with the OD measurement.

#### 7.4 Discussion

The results of the measurements presented here permit some considerations to be made about the processes which are occurring in the irradiated Optical density 305 nm



Fig. 37 The correlation between the increase in the third species and the decrease of the second species in P2 on exposure to 320-390 nm light.

Fig. 38 The change in the photo-induced ESR spectrum in P2 on exposure to 320-390 nm light. a) after 9 days in 340-390 nm light in vacuum, b) after 2 days in 320-390 nm light in air, c) after 5 days in 320-390 nm light in air.

PMMA and which are responsible for the photosensitive effect.

The exposure to 340-390 nm light reveals that the initial species formed on irradiation, and giving the typical nine line ESR spectrum and OD spectrum, fades and that a second species is formed which absorbs in the 300 nm region. This second species is correlated with the fading of the initial species and, as the total radical concentration remained constant, within the experimental error of the measurement, during the exposure, it is also correlated with the development of the second ESR spectrum and is thus most probably a radical species.

cm <sup>3</sup> )
66.5
65.0
68.4
69.7
42.9
42,6

Table 4. The total radical concentration following

different exposures to 340-390 nm light

An analysis of the fading of the initial species reveals (Fig. 39) that the fading follows an equation of the form

 $R_{t} = R_{0} e^{-\alpha t}$ (4)

Initial radical

concentration (p-p)mm

Initial radical

concentration (p-p)mm

200 200 b а 150 150 100 100 2.8 Mrad 2 Mrad 50 50 1 Mrad Ρ2 20 20 **P1** 10 10 2 4 6 8 2 6 8 10 4 10  $(light exposure)^{1/2}(h)^{1/2}$  $(light exposure)^{1/2} (h)^{1/2}$ 

Fig. 39 The fading kinetics of the first radical species on exposure to 340-390 nm light. a) in Pl and P2, b) in P2 at different radiation doses.

where  $R_0$  is the initial radical concentration,

- $\boldsymbol{R}_{\star}$  is the radical concentration at time t,
- t is the exposure time,
- a is a fading coefficient.

This type of fading kinetics has previously been found for radicals in PMMA following heat treatment (Campbell & Looney, 1962; Michel et al., 1967). An attempt to analyse the curves into two separate exponential components was not successful. This equation is purported by Campbell & Looney (op. cit.) to describe a second order diffusion controlled process and is considered in more detail in the Appendix.

In this respect, Campbell & Turner (1968) mention a first order process of photo-induced radical conversion in polyethylene terephthalate and Dole & Böhm (1966) found a first order decay of radicals in polyethylene at  $-196^{\circ}C$ on exposure to light. Dole & Böhm suggest a process of hydrogen atom migration, although they do not rule out the possibility of charge transfer. The second order diffusion controlled process found here, whilst different in nature to that found by Dole & Böhm, would be in line with the process of hydrogen atom migration.

The second ESR spectrum developed on exposure to the 340-390 nm light appears to be a broad singlet with some structure. This spectrum may represent the species which gives the optical absorption at 300 nm, or it may be the total of several superimposed spectra, one of which represents the species giving the absorption at 300 nm. It has not been possible to isolate the new ESR spectrum from the original nine line spectrum and consequently no identification has been attempted. In any case, the new ESR spectrum bleaches without changing shape and the fading kinetics of the 300 nm absorption, obtained from Fig. 37, shown in Fig. 40, indicate a first order process which suggests dissociation. The formation of the stable OD component from a dissociation process on irradiation has been proposed in Chapter 4.

One major difference between the stable OD component formed on irradiation and the third species on the bleaching of the second species is that the third species does not exhibit any photoluminescence. This may be an inherent difference, or it may be due to the quenching effect caused by all the radiation and light degraded products formed by the extensive treatment of the irradiated samples. In spite of this difference, the stable component formed on irradiation and the third species are considered to be the same product. Unstable OD 305



Fig. 40 The fading kinetics of the second radical species in P2 on exposure to 320-390 mm light.

The photosensitive effect found in the irradiated PMMA in these experiments may be summarized in the following equations:

R1 + hv (340-390)  $\longrightarrow$  R1<sup>X</sup>

 $R1^{\times} + B \longrightarrow R2 + other species$ (diffusion controlled)

R2 + hv (320-390 nm)  $\rightarrow$  R2<sup>X</sup> + S1 + other non-radical species (dissociation)

where R1 is the first radical species,

R2 is the second radical species,

and S1 is the stable component or third species.

Table 5 summarizes the physical parameters which may be associated with R1, R2 and S1.

In view of the results of Alexander et al. (1954) on the radiolysis of PMMA it seems reasonable to suspect that some of the non-radical species formed in the light treatments are gases such as  $H_2$ ,  $CH_4$ , CO and  $CO_2$ .

This photosensitive effect is the most important effect from the point of view of the use of PMMA for dosimetry. Depending on the exposure, it can be extremely large and can lead to a considerable over-estimation of dose. It is not possible to choose a wavelength for dose measurements such that the light effect can be avoided. It is however possible to check for a photosensitive effect by comparing the OD measured at two wavelengths, for example 300 and 330 nm, with the relationship at these wavelengths for a

Species	ESR spectrum	OD spectrum	PL emission	$\frac{\text{Stal}}{\text{O}_2}$	temp.	Comments
Irradiation induced stable OD component	none	no peak > 260 nm OD increas- ing rapidly below 280 nm	440 nm	+	+	
Fresh irradiated unstable OD component, Rl	9-line	broad, 250- 400 nm peak 275-280 nm	560-580 nm	-	fades above 70 <sup>0</sup> C	decays under UV light
2nd para- magnetic species, R2	associated with broad singlet	broad peak at 300 nm	520 nm	-	fades above 70 <sup>0</sup> C	formed under UV light also bleach- ed
3rd species S1	none	OD increasing rapidly below 280 nm	none	+	+ to 150 <sup>0</sup> C	formed under light, not bleached by light above 340 nm

Table 5. Survey of the physical parameters associated with different species found in irradiated PMMA on exposure to light.

freshly irradiated unaffected sample.

It is concluded that the photosensitive effect arises from a photoinduced conversion of one radical into one or more new radicals by a second order diffusion controlled process. Further light exposure can lead to a bleaching of the second radical and an increase in the stable component. This effect is most important in radiation dosimetry.

## 8 The effect of heat

#### 8.1 Introduction

The treatment of PMMA at different temperatures offers the possible resolution of the different species formed on irradiation. Boag et al. (1958) have mentioned the effect of temperature on the OD of irradiated PMMA and have found a strange effect, namely, that at low doses there was an increase in OD and at high doses the OD faded, and the balance point was dependent on temperature. In the field of ESR measurements on PMMA, the temperature treatments have led to a considerable amount of disagreement and confusion (Symons, 1963; Bullock & Sutcliffe, 1964; Michel et al., 1967).

Some measurements have been made to study the effect of temperature on the irradiated PMMA, but on the whole the results, whilst giving some additional information, do not permit an accurate resolution of all the species formed and processes which are occurring.

#### 8.2 The effect of increasing temperature on the OD

Samples of P1 type PMMA, irradiated to different doses, were exposed to a fixed temperature for 5 min, measured at 295, 307, 314 and 350 mm, and then exposed to a temperature  $10^{\circ}$ C higher than the initial temperature, were measured, and so on until  $200^{\circ}$ C was reached, at which temperature the samples were no longer handleable. The results are shown in Fig. 41 for the four wavelengths. At 295 and 307 nm the OD increases slightly with temperature up to  $60^{\circ}$ C, at 314 nm the OD remains constant, and at 350 nm the OD decreases slightly. The reason for this effect is made clear in 8.3. At temperatures above  $60^{\circ}$ C the OD begins to fade at all wavelengths, although it is barely noticeable at the lowest dose measured, 250 krad. At  $110^{\circ}$ C a minimum in the OD is reached and, as the temperature increases, the OD increases slowly until, at 200°C, the 2 Mrad sample foamed. It is important to note that the stable OD at the minimum is greater than the value expected for the OD component stable to oxygen. If samples are exposed to  $120^{\circ}$ C for 10 minutes after Optical density

Optical density



Fig. 41 The effect of increasing temperature on the OD. a) P1 irradiated to 870 krad, at different wavelengths. b) P1, at 314 nm at different doses.

irradiation the stable value obtained is intermediate between these values, and if samples are exposed to  $150^{\circ}$ C for 1 minute the oxygen stable value is obtained (Fig. 42). It would appear that the unstable OD component, or radical, is temperature sensitive, but that the stable component is formed or developed on slow heating, but not on rapid heating. Thus an analysis of the fading of the OD at a fixed temperature is confused by the development of the stable OD.

8.3 The change in the OD spectrum with temperature

The OD spectrum of P1 and P2 samples of PMMA have been measured following exposure to a temperature of 55°C. The results are shown in Figs. 43 and 44 and indicate that the OD increases between 280 nm and 315 nm and decreases on either side of these values. If these results are compared with the results of the exposure to UV light, it may be seen that the original OD

#### **Optical density**







Optical density



spectrum is fading and that the second species is formed to a small extent giving the increase in the 300 nm region of the spectrum.

If, after the 55°C treatment, the samples are heated at 75-80°C, the complete OD spectrum decreases indicating that the first species continues to fade and that either the fading occurs via a different process which does not involve the formation of the second species, or that the second species is formed but is also fading and that a balance between the formation and fading results in no change in the spectrum shape. There is no experimental evidence in favour of either one of these possible processes.

#### 8.4 Discussion

These two experiments are somewhat complimentary in that the change in the OD spectrum on warming reflects the results of the first experiment. The results, coupled with those from the light bleaching experiments, give some extra information on the processes which are occurring. The change in spectrum indicates the slight development of the second radical species more obviously found following exposure to 340-390 nm light, and a change in ESR spectrum in PMMA has been found on warming at  $55^{\circ}$ C (Bresler, 1959), which corresponds with the OD spectrum change found here. In addition, the first radical species has been found to fade via a second order diffusion controlled process both on heating (Campbell & Looney, 1962; Michel et al., 1967) and on light exposure. It is also interesting to note that Barnes et al. (1969) have found a temperature induced electric conduction process in irradiated PMMA. The conduction process occurred in the range of  $60^{\circ}$ C, and was found to be caused by a positive charge carrier. The association between the conduction process and the change in the ESR and OD spectra is not clear.

The results presented here also indicate why the most reliable wavelength for radiation dosimetry using optical density measurements has previously been found to be 314 nm (Chadwick, 1969; Chapter 4). Any temperature variations during the irradiation and storage of a dosimeter before measurement will manifest themselves in small changes in the OD spectrum, but in the wavelength region 310-320 nm, where the changes compensate each other and the OD change is still a useful measure of radiation dose, the relative variations will be minimal.

### 9 General discussion

It is not the intention of the work presented here to investigate the primary processes occurring on irradiation which lead to the eventual formation of the nine line ESR radical, but to study the use of optical and microwave techniques in an analysis of the eventual radiation products and the changes which occur in these products when post irradiation treatments are applied. In general, it may be concluded that these techniques can be combined to give more information than when they are applied independently. For example, the ESR technique is necessary to show that light exposure of the irradiated sample leads to the fading of the initial species which is masked in the optical measurements by the development of the new species. On the other hand, the optical measurements indicate the existence of a stable species which cannot be measured by the ESR technique. The results of the work presented here, some of which are reviewed in a more general sphere in the following sections, have illustrated the advantages of combining two or more analytical techniques in a study of this kind and are of use in practical radiation dosimetry, as they illustrate various phenomena which can occur to cause large errors in the measurement of radiation dose using clear PMMA.

#### 9.1 The optical density - dose relationship

The unstable OD component has been correlated with the nine line ESR signal arising from the radical. The dose relationship of the radical for gamma rays and for fast neutrons has been shown to follow an equation of the form

$$R = k (1 - e^{-\phi D})$$
<sup>(5)</sup>

which has been developed from a hypothesis based on radical production and annihilation. The coefficient  $\phi$  describes the probability that a radical is annihilated by the radiation. The literature contains many references to a radical-dose relationship described by a similar equation for both gamma

rays and higher LET radiation (Müller, 1963; Rotblat & Simmons, 1963; Casteleijn et al., 1964; Köhnlein & Müller, 1964; Müller, 1964; Müller & Köhnlein, 1964; Müller et al., 1964; Henriksen, 1966a; Stratton, 1967), and Horan & Snipes (1967,1969) have recently shown the direct annihilation of radicals in alanine, valine and other materials of biological interest. Ten Bosch (1967) has also considered the various radical-dose relationships which arise from different models and determined experimentally that in collagen the best fit was given by an equation having the same form as (5).

In all the samples mentioned above, including the PMMA samples, the subject of the investigation was solid material in the dry state, in most cases biochemicals. In radiobiological work with dry enzymes and bacteriophage the biological samples may be considered to be in a similar state but biological material such as cells, pollen, plants and animals are not in a solid state and are not completely free of water, and the physical state may be better compared to a gel or solution (Stein & Tomkiewicz, 1970).

In comparing, and applying, the results for PMMA and other solid materials, and the hypotheses developed to explain the results, to radiobiological work, it is necessary to bear this phase difference in mind. In a gel or solution, the diffusion processes may well become important and radical-hydrogen abstraction effects, or radical-radical recombination effects, may well dominate the radical-dose relationships and influence the shape of the curve. The hydrogen abstraction theory has been developed by Braams (1963) and in gels, when the diffusion of small particles will be easier than in solids, this process could be dominant. In solutions where complete diffusion of bigger units and radicals is possible, the effect promises to be very complicated, with various processes competing with each other.

Free radicals are considered to be responsible for at least part of the biological effect of radiation and some correlations have been made in the case of enzyme inactivation (Brustad et al., 1966; Henriksen, 1966a; Henriksen, 1966b). In radiobiological work it is often supposed that the radicals are responsible for the modifiable part of the radiation effect (Dertinger & Jung, 1970). Higher LET radiation is said to create more unmodifiable damage so that the radiobiological effect cannot be influenced to the same extent as following gamma radiation. The results in PMMA, in agreement with others in biochemicals, indicate that, following high LET radiation at the same rad dose. Thus, following high LET radiation, the unmodifiable part of the damage may

well be quantitatively greater but the radical concentration, and thus the modifiable part of the damage, may well be quantitatively less than that found following an equivalent gamma radiation. It is not evident, from the results presented here, what the unmodifiable part of the damage is, nor how it can be measured physically.

#### 9.2 The identification of the initial ESR spectrum

In view of the differences reported in literature concerning the identification of the initial ESR spectrum, it is interesting to compare the changes in the ESR spectrum found on exposure to light with the various spectra found in literature which lead to a discussion about whether, or not, the initial spectrum is made up of one or two different radicals.

The experiments which have led some authors to conclude that two radicals contribute to the initial nine line ESR spectrum have involved either, warming of an irradiated sample at 80°C (Abraham et al., 1958; Campbell & Looney, 1962; Symons, 1963; Bullock & Sutcliffe, 1964; Michel et al., 1967) or, a variation in the initial spectrum dependent either on the method used to produce the radicals or on the method used to prepare the samples (Bullock & Sutcliffe, 1964; Ormerod & Charlesby, 1964; Michel et al., 1966).

Examination of the different spectra published in the literature indicate that the form of the modified spectra are always very similar in form to that found on exposure to light (Fig. 33). In Chapter 9, heating of the irradiated PMMA is shown to change the OD spectrum in a way which suggests the slight development of the same species as is formed on light exposure, and this would explain the change in ESR spectrum on heating at 80°C. The kinetics of the decay of the initial spectrum at 80°C has been found to be the same as that found on light exposure (Campbell & Looney, 1962; Michel et al., 1967) and thus the initial reaction of the radical R1 on heating may probably be written as

#### R1 + heat $\rightarrow$ R1 + B $\rightarrow$ R2 + other products (diffusion controlled)

It is most likely that at  $80^{\circ}$ C the second radical R2 is also unstable and in this respect the light induced radical giving the peak optical absorption has been found to fade at  $70^{\circ}$ C. Thus a build-up of R2 radicals has not been found in ESR experiments on heating because the above reaction equation should by completed by
#### R2 + heat $\rightarrow$ other products

and the concentration of R2 will be in a balance between production and decay.

At  $110^{\circ}$ C, Symons (1963) found no change in the ESR spectral shape on fading and this suggests that at these higher temperatures other processes, occurring at a higher rate than the diffusion process which converts R1 to R2, may be responsible for the decay of R1 radicals. This explanation would also account for the results shown in Fig. 42, which indicate that at lower temperatures more stable component is formed than at high temperatures if

### R2 + heat $\longrightarrow$ S1 + other products

The variation in initial spectrum, dependent on the method used to produce the radicals, also suggests that more than one radical species results from the irradiation. The discussion in the literature has always been concerned with one radical giving the nine line ESR spectrum or one five line spectrum superimposed on a four line spectrum arising from two radicals. The work of Abraham et al. (1958), Symons (1963), Fischer (1964) and Kourim & Vacek (1965) is very positively and convincingly in favour of the nine line spectrum arising from only one radical.



The results of Michel et al. (1966) and ten Bosch (private communication, 1971) indicate very clearly that this nine line radical is associated with the presence of excess monomer and could be the monomer radical. When monomer-free PMMA is irradiated, a different spectrum is obtained which resembles a composite nine line plus a broad singlet spectrum. The result found in Chapter 7, whilst revealing the conversion of one radical species into other radical species is also not in favour of a five and four line spectrum as the spectrum which is developed, although developing at the position of the centre two lines of the supposed four line spectrum, does not indicate any development at the position of the outer two lines of the supposed four line spectrum.

It is however suggested that the difference in the spectrum found when the radicals are produced by different methods may be accounted for by the presence of two radicals, namely, the normally found nine line ESR spectrum plus the radical giving the broad singlet which can be developed by light exposure of an irradiated sample. The balance between the two radicals may be affected by numerous factors and it is not clear from the results presented in this work if the radical giving the broad singlet must always be developed from the radical giving the nine line ESR spectrum, or if it can be formed independently. In any case, the results of the effect of light exposure on R1 indicate that the radical spectra produced by photo-dissociation of the polymer will probably be made up of a contribution from both R1 and R2 in a different ratio to the spectra produced by  $\gamma$  irradiation of the polymer.

The broad singlet ESR spectrum has been found by Michel et al. (1967) following extended heating at 80°C, and even the spectrum shown by Bullock & Sutcliffe (1964) to represent the four line spectrum can be analysed into a broad singlet with a very small contribution of the original nine line spectrum superimposed on the singlet.

#### 9.3 The photo-induced process

The results presented in Chapter 7 lead to a series of relationships which describe the effect of light on the irradiated PMMA. At this stage, any further description of the process would be based on speculation, and a chemical study of the effect is necessary to provide a sound base for further considerations of the physico-chemical processes involved in the radical conversion. However, it can be stated briefly here, that further considerations must start from the initial radical, which has been identified as

$$R1 = M - M - CH_3 - C \cdot$$

$$COOCH_3$$

$$COOCH_3$$

$$CH_3 - C \cdot$$

$$CH_3$$

where M is the monomer unit

and explain the following facts:

(1) the decay of the initial radical occurs via a bimolecular diffusion controlled process;

(2) the total radical concentration does not change;

(3) a stable product is produced which is identical to that found following gamma irradiation;

(4) the new radical, or one of the new radicals, has an intense OD absorption at 300 nm;

(5) the new radical, or radicals, have an ESR spectrum which resembles a broad singlet with some structure;

(6) the process should also occur to some extent on heating to 80°C.

9.4 The application of clear polymethylmethacrylate in radiation dosimetry

Clear polymethyl methacrylate is increasingly used as a radiation dosimeter in the range 100 krad to 10 Mrad in food irradiation, radiation sterilisation of medical products and radiation technology using large gamma irradiation plants or electron generators. It is being used by the United Kingdom Panel on Gamma and Electron Irradiation and the American Society for Testing and Materials for dose intercomparison in national laboratories and may soon be used for dose intercomparisons in gamma irradiation plants by the IAEA.

The work presented in this thesis indicates that clear PMMA may be used to determine radiation doses in the 100 krad to 10 Mrad range accurately by measuring the OD change at a wavelength in the neighbourhood of 314 nm, if certain precautions are taken. The optical density change is made up of two components following irradiation; a stable component and an unstable component which is shown to be caused by a radical. The dose relationship is nonlinear and begins to saturate at high doses. It has also been shown that a pretreatment of the PMMA samples to remove the molecular oxygen present in the plastic matrix leads to an initially linear OD-dose relationship from the origin so that the pretreated PMMA can be used for dosimetry between

30 krad and 300 krad and thus extends the useful range of the dosimeter.

The radical can be affected by oxygen and fades, by light to produce a second radical species which drastically alters the OD at 314 nm, and by heat which initially alters the OD spectrum but has a minimal effect in the neighbourhood of 314 nm, whereas extended heating above  $70^{\circ}$ C causes a fading of the OD. The effect of light and heat can also lead to a change in the level of the stable OD component. If necessary the stable OD can be used as a recheck of a dose measurement following complete oxygen diffusion, but in order to achieve this in a reproducible way the PMMA samples should be stored in the dark at  $15^{\circ}$ C to prevent light and heat effects from altering the stable OD level.

Consequently, for accurate radiation dosimetry the wavelength of 314 nm is to be preferred because it is sensitive for the lower doses and minimises errors arising from changes in the OD spectrum caused by temperature variations. Exposure of the irradiated sample to light should be avoided, as this can cause the most serious changes in the OD, and measurements should be made within a few hours of the irradiation to avoid fading effects caused by oxygen diffusion.

#### 9.5 Suggestions for further studies

The results of this study, which indicate that the combination of different techniques to investigate certain phenomena can give a more detailed picture of the phenomena, lead, however, to more general conclusions about future research into similar problems.

It is clear that, especially in the study of the light effect on irradiated PMMA, the results cannot be completed to give a full description of the radical conversion process without some further experimental work on the organic chemistry of the process. Thus, the general suggestion which can be made is that a combined multidisciplinary investigation of problems of this nature would lead to a more detailed and complete picture of the process and a better understanding of the mechanisms involved.

In particular, an interdisciplinary approach involving physical, physico-chemical and organo-chemical measurements on the mechanism involved in the radical annihilation by radiation (Horan & Snipes, 1967; 1969; 1971; Henriksen, 1971) will lead to a better understanding of the processes involved in the annihilation.

In the programme planned at the Institute for Atomic Science in Agri-

culture to study the primary radiation interactions in biochemicals, a complementary biochemical investigation of the results of the radiation interactions together with the physics investigations would give more rewarding information.

## Appendix

The second order diffusion controlled reaction process

The theory of the kinetics of colloid coagulation as a diffusion controlled process was originally developed by Smoluchowski (1915,1917) using Fick's law of diffusion. The theory is based on the assumptions that around one of the reactant particles a concentration gradient for the other species is set up and that the rate of flow of particles in this concentration gradient is governed by Fick's law of diffusion. The fundamental differential equation

$$\frac{\partial c}{\partial t} = Dv^2 c \tag{i}$$

is solved with the boundary condition c = o on the surface of a sphere of radius R. Assuming this boundary condition and a uniform initial concentration of the diffusion species of  $C_o$  at t = o, the flux of the diffusing particles across the sphere at r = R is

$$\theta = 4\pi R^2 D \left(\frac{\partial C}{\partial r}\right) r = R$$

which leads to

$$\theta = 4\pi DRC_{o} \left(1 + \frac{R}{\sqrt{\pi}Dt}\right)$$
(ii)

This theory has been considered by Collins & Kimball (1949) and Waite (1957,1958) has derived a similar equation based on a more general approach to the problem of factors governing the rate of a bimolecular chemical reaction. Waite obtains the equation

$$\frac{dC_{A}}{dt} = \frac{dC_{B}}{dt} = -4\pi r_{O} D \left\{ 1 + \frac{r_{O}}{(\pi D t)^{\frac{1}{2}}} \right\} C_{A} C_{B}$$
(iii)

for a diffusion limited reaction between two molecular species A and B having a uniform initial distribution and reacting in such a way that the species A may be considered to be surrounded by a sphere of influence  $r_{c}$ 

such that any particle of species B diffusing within this sphere reacts instantaneously with the particle of species A. In (iii)

- $C_A$  is the concentration of species A at time t
- ${\rm C}_{\rm B}$  is the concentration of species B at time t
- D is the diffusion coefficient of species B
- $r_0$  is the radius of sphere of influence.

One solution of equation (iii) given by Waite is, in the case that  $C^O_A$  =  $C^O_R$  when

$$\frac{1}{C_{A}} = \frac{1}{C_{A}^{0}} + K \left\{ 1 + \frac{2r_{o}}{(\pi Dt)^{\frac{1}{2}}} \right\} t$$
 (iv)

The experimental points given in Chapter 7 do not fit this equation. • The equation (iii) has been simplified by Campbell & Looney (1962) by making two basic assumptions:

> 1. that  $C_B^0 >> C_A^0$  and is constant 2. that  $\frac{r_0}{(\pi D)^2} >> 1$ ,

so that the equation can be reduced to

$$\frac{dC_A}{dt} = -4\pi r_0 D \left\{ \frac{r_0}{(\pi Dt)^{\frac{1}{2}}} \right\} C_A C_B^0$$
 (v)

Integration gives

where a

$$C_{A} = C_{A}^{o} e^{-\alpha \sqrt{t}}$$
 (vi)  
= 4  $r_{a}^{2} C_{D}^{o} (\pi D)^{\frac{1}{2}}$ 

The kinetics of this equation are in fact first order, but as it is a diffusion controlled process two different species must be involved.

The basic assumptions made by Campbell & Looney are only justified by the good fit between the experimental points and equation (vi) shown in Fig. 39 and found by Campbell & Looney and Michel et al. (1967) for the temperature induced fading of radicals in PMMA.

The coefficient  $\alpha$  contains  $C_B^0$ , the initial concentration of the diffusing species B and has been found in Fig. 39 to be independent of radiation dose and type of PMMA. This implies that either the species B is formed on radiation but saturates at a low dose or that it is inherent in the PMMA as a contamination such as monomer, initiator fragments or possibly a gas.

# Summary

The induction and stability of an optical absorption band in the near UV region found in clear polymethyl methacrylate following irradiation has been studied using optical and electron spin resonance techniques.

The effect of increasing gamma and fast neutron radiation dose on the development of the optical density has been measured and the optical density has been shown to be made up of an unstable and a stable component. The use of different LET radiation has been shown to influence the optical density dose relationship. An analysis of the optical density - dose relationships has been made in terms of radical production and annihilation and fragment production and annihilation. The complete model used in the analysis predicts that the radical concentration should decrease at very high dose levels, an effect which has been found by others in biochemicals. The unstable optical density component has been correlated with the typical nine line electron spin resonance spectrum found in irradiated polymethyl methacrylate.

The photosensitive effect found in irradiated polymethyl methacrylate has been studied and has been shown to be caused by a free radical conversion process which also causes an increase in the stable optical density component. The same process, though occurring to a lesser extent, is considered to be responsible for the change which occurs in the optical density and electron spin resonance spectrum on warming.

It is concluded that the induced optical density change in clear polymethyl methacrylate can be used as an accurate high level radiation dosimeter system for gamma and electron irradiation when certain precautions are taken in handling the dosimeters and when

(1) the measurement of induced optical density change is made at a wavelength of 314 nm,

(2) the exposure of irradiated dosimeters to light is avoided,

(3) the optical density - dose relationship is not assumed to be linear but is calibrated.

It has been demonstrated that the combination of measuring techniques

within one discipline has led to a better understanding of the phenomena than could be reached by using one technique alone, but it is proposed that for the investigations of similar problems an attack at a multidisciplinary level is most desirable.

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# Curriculum vitae

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