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Advanced radiation chemistry research: current status

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FOREWORD

Radiation chemistry is a branch of chemistry that studies chemical transformations in materials exposed to high-energy radiations. It is based on the use of ionizing radiation as the initiator or catalyst in chemical reactions.

Practical applications of radiation chemistry today extend to many fields, including health care, food and agriculture, manufacturing, and telecommunications. The range of contributions from this, largely hidden, branch of science is not widely known.

The most significant advantage of radiation chemistry lies in its ability to be used in the production and study of almost any reactive atomic and molecular species playing a part in chemical reactions, synthesis, industrial processes, or in biological systems. The techniques are applicable to gaseous, liquid, solid, and heterogeneous systems. By combining different techniques of radiation chemistry, the reaction mechanism and kinetics of chemical reactions can be studied.

Over the last few years a number of meetings have taken place, under the auspices of the IAEA, in order to evaluate recent developments in radiation chemistry as well as the trends indicated by the results obtained. Radiation chemists from different countries have participated at these meetings.

The present publication, a companion to the previous publication — *New Trends and Developments in Radiation Chemistry, IAEA-TECDOC-527 (1989)* — includes some of the important contributions presented at these meetings. It is hoped that it will provide a useful overview of current activities and of emerging trends in this field, thus promoting better understanding of potential contributions of radiation chemistry to other fields of knowledge as well as to practical applications in industry, medicine and agriculture.

EDITORIAL NOTE

In preparing this publication for press, staff of the IAEA have made up the pages from the original manuscripts as submitted by the authors. The views expressed do not necessarily reflect those of the governments of the nominating Member States or of the nominating organizations.

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CONTENTS

INTRODUCTION

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1. BACKGROUND

The contributions presented in this publication show that new fundamental knowledge gained in the course of recent applications of radiation chemical methods is of great significance to a number of diverse areas of basic and applied chemistry, biology and physical chemistry. The fundamental knowledge of radiation chemistry, as demonstrated in these contributions, has found a number of different applications in industry.

Particular interest of industry has been in radiation modification of polymers for different uses. Radiation sterilization of medical products, cosmetics, pharmaceuticals and their raw materials, is largely based on the knowledge and data provided by radiation chemistry. New developments in biochemical applications have recently occurred. Radiation chemistry of gases has become the subject of increasing interest due to potential use of radiation processing for removal of toxic components in flue gases. New developments are likely to occur in fundamental studies of polymeric systems, biological systems, and others.

Nevertheless, the radiation chemical community is still relatively small. There are today, worldwide, only a few hundred active investigators in basic research and, perhaps, a similar number in the radiation processing industry. This regrettable state results from the fact that active practice requires the availability of major, fairly sophisticated and expensive equipment, such as high energy electron accelerators or gamma sources. Therefore, most of the interest is concentrated in "national" laboratories and institutes, rather than in universities. Most chemistry faculty members and graduate students are, in fact, unaware or only distantly aware of the contributions that radiation chemistry methods can make to their studies. At the same time, it must be recognized that the impact of radiation chemistry is quite diffuse and often information obtained by radiation chemical methodology is not recognized as such.

2. OBJECTIVES OF THE MEETINGS

A number of consultants meetings were convened by the IAEA, with the main objective to review new developments and trends of research in radiation chemistry, thus allowing it to reevaluate its role in promoting the advancement of radiation chemistry research in its Member States.

3. SHORT SUMMARY OF INDIVIDUAL CONTRIBUTIONS

Seven of the important contributions presented at these meetings are reported here in full text. They do complement many of the studies presented at the Bologna Advisory Group Meeting (see IAEA-TECDOC-527 of 1989), and demonstrate that, indubitably, radiation chemistry methods have now a broad range of applications.

The contribution of *von Sonntag* reviews trends in fundamental research in radiation chemistry of aqueuos solutions, pointing out a number of fields that are especially challenging and where future research effort might be particularly well rewarded. After discussing techniques for converting primary water radicals into radicals of interest, special attention is given to peroxide radicals, and to free radical chemistry of nucleic acids, proteins, carbohydrates, lipids and sulfur compounds, which can be useful in the fields indicated. Studies on unusual oxidation states of transition metals, such as Fe and Cu, are briefly mentioned, and so are their great potential applications.

Phillips and Deeble review new lines of research that have led to an increase in the scope and versatility of existing radiation processing as well as to the development of new techniques. They reserve their presentation to the analysis of the contribution of radiation research to several areas, one important being radiobiology. First addressed is the contribution in the development of radiosensitising drugs to be used in cancer radiotherapy. Next is its utility in enhancing radiation properties in materials used for packaging and for manufacturing medical disposable products, to be radiation sterilized, as well as in biomaterials and in tissue replacing materials. Its contributions to better understanding of atmospheric chemistry is examined and so are its uses in developing dosimetric systems. The widespread occurrence of free radicals in chemical and biochemical systems is considered, demonstrating the advantages of radiation chemistry research in elucidating properties of these reactive species, in the case of peroxidation processes and hyaluronic acid degradation; also discussed is the use of radiation chemistry in the study of high temperature effects in coolant water, employed in nuclear plants, as well as of radiation induced corrosion and dissolution of metal oxides in such systems.

Charlesby reviews recent applications of radiation chemistry in several other fields, dealing foremost with its effectiveness in studying radiation-induced main chain scission in polymers, in studying crosslinking and network formation, as well as its usefulness in examining the effects of radiation in the course of polymerization, graft polymerization, polymerization in solutions, and curing of polyesters. He examines potential applications of radiation chemical research to produce fire- and radiation resistant polymers, new composite materials and polymers of higher strength, to achieve composite three-dimensional structures difficult to attain in other ways, to produce foamed materials with controlled pore size and to produce grafted films for chemical control such as catalysts. Many other highly rewarding potential applications are also discussed.

Tabata summarizes the spatial distribution of radicals, generated by various kinds of radiations in organic compounds, and after introducing earlier work on LET effects in polymers, discusses several new recent results on LET effects, like transient phenomena. Helium gas, water, KCN, and organic compounds, including biological molecules and polymers, are cited as the target materials, in gaseous, liquid and solid phases. The fact that high LET radiation is characterized by high levels of excitation, nuclear recoil processes, and high densities of excitation, gives rise to very specific chemical reactions in target materials, emphasizing that LET radiation chemistry is developing into a fascinating new field of science.

Hoffman reviews recent studies employing radiation chemistry in the synthesis or modification of polymeric components of biomedical implants and devices, with special emphasis on surface modification (physico chemical and biological), on polymerization, and on bulk property modification.

Garnett, Dworjanyn, Bett and Dang discuss the usefulness of radiation chemistry in the study of the role of novel additives in accelerating graft processes intitiated by both ionizing radiation and UV, referring in particular to additives such as mineral acids, specific organic compounds like urea, inorganic salts and polyfunctional monomers, particularly acrylates. They propose a unique mechanism for the function of these additives. They discuss the value of the finding that common additives are shown to accelerate both grafting and curing processes, initiated by electron beams and by high pressure UV lamps, for observing concurrent graft with cure. The mechanistic contribution of ions to the currently accepted free radical process for both grafting and curing, initiated by ionizing radiation, is considered from basic studies with Fourier Transform ion cyclotron resonance mass spectrometry.

Hill reviews the studies of radiation chemistry in the field of polymers with special reference to the relationships between polymer structure and sensitivity towards high energy radiation, including Co-60 gammas, electron beams and UV light. Results are discussed on the effects of radiation on polymers containing carboxyl groups, acrylate groups, sulphone groups, amide linkages and aromatic residues.

4. MAIN CONCLUSIONS

The main conclusions from these reviews and discussions confirm those of the Advisory Group meeting in Bologna (1989), with regard to the necessity to integrate the information derived from radiation chemical investigations into the various traditional branches of chemistry, in order to gain maximum benefit from the advances made in recent years in radiation chemistry, and that the benefits of successful industrial application of radiation technology derive directly from the wider investment in radiation chemical investigation. It is expected that this publication will contribute towards this goal.

TRENDS OF RESEARCH IN RADIATION CHEMISTRY

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Abstract

In the present paper the radiation chemistry of aqueous solutions is reviewed. Areas of active research are pointed out and an attempt is made to assess future research trends in this field. Special emphasis is laid on fundamental aspects, rather than on technical applications. Thus the versatility of the pulse radiolysis technique is briefly described. The primary processes occurring in the radiolysis of water are presented and techniques for converting the primary water radicals into radicals of interest are discussed. Special chapters deal with peroxyl radicals, as well as with the free radical chemistry of nucleic acids, proteins, carbohydrates, lipids, and sulfur compounds. Studies on unusual oxidation states of transition metal ions are briefly mentioned.

1. Introduction

In the present paper, trends in the *fundamental research* in radiation chemistry (aqueous media) will be discussed. We will also try to identify fields that are especially challenging, and where further research effort might be particularly well rewarded.

In the early days of radiation–chemical research, the progress of our knowledge with regard to chemical transformation was closely linked to the determination of stable end products; any intermediates such as radiation–induced free radicals had to be inferred from such data. With the advent of studies in frozen systems, such as the detection of the solvated electron in frozen solution [1], a new area was opened up, the detection and identification of free–radical intermediates by optical and ESR spectroscopy. In the early sixties, the development of pulsed radiolysis led to a complete shift of emphasis. It became possible to follow the formation and decay of intermediates as a function of time by a variety of detection techniques. The radiolysis mechanism of water became well–established and was eventually developed into a beautiful and unparalleled tool to investigate free–radical reactions in this solvent [2, 3]. With the increasing availability of pulse radiolysis facilities, a large body of information on the *kinetics* of free–radical intermediates has been built up since then, and at present effective research in radiation chemistry without access to pulse radiolysis

facilities is not possible. Pulse radiolysis is an expensive tool and most radiation research groups are rather small. As a consequence, a very important aspect has often been neglected, namely, the quantitative analysis of the radiation *products*. Hence compared with the situation in the early days of radiation chemistry, in a sense the situation is reversed, for we now know a lot about various properties of intermediates but relatively little about the ensuing products. But in the recent past there has been enormous progress in analytical chemistry. This now allows speedy and accurate analysis of radiation products which are usually present at low concentrations only. Accordingly, there is reason to hope that in the near future there will be a general trend to combine in the same system pulse radiolysis and product study.

It is evident that pulse radiolysis will remain a major tool in the future. The state of the art and future trends in this area have been reviewed recently [3–10] (the latter review having appeared in an IAEA report). Nevertheless, a brief comment as to new techniques for the detection of transients is in order here.

We have already said that it is the goal of the present review to point out some active areas of *fundamental research* in radiation chemistry. These are often linked to more applied subjects such as radiotherapy (radiation biology), radiation bioengineering, polymer sciences, food technology and environmental sciences. Technical applications of radiation will be dealt with in another article in this Volume, but reference will be made to the relevant applied field where appropriate.

A further restriction must be imposed: in this brief review only developments in the radiation chemistry of aqueous solutions will be dealt with. Organic solvents, solids and the gas phase are omitted. Even then, only a selection of topics in the large field of aqueous solution radiation chemistry can be addressed, and this article remains far from exhaustive. A recent publication on the development of radiation chemistry over the last few years [11] is largely devoted to other aspects than those discussed here.

2. Pulse radiolysis

Pulse radiolysis is one of the most powerful tools in studying free–radical reactions. A short pulse of high–energy electrons is delivered to a cell filled with a solution to be investigated. Sub–microsecond pulses are now standard. Most of the kinetic data which became available from radiation–chemical studies have been obtained by this method.

Many different techniques are now available to detect transients generated by these methods [10]. They comprise UV/VIS spectroscopy, conductometry,

light–scattering, polarography, Raman spectroscopy, electron spin resonance (ESR) spectroscopy, Fluorescence–detected magnetic resonance (FDMR) spectroscopy, and chemically–induced nuclear polarization (CIDNP) spectroscopy. Pulse radiolysis can also be combined with a rapid–mixing device which allows long–lived radicals to react with added substrates also under conditions of high additive concentration. In a normal pulse radiolysis experiment, such high additive concentrations would otherwise have scavenged the precursor radicals of the long–lived intermediates to be investigated. Opaque samples may be investigated using diffuse reflectance [12].

From this brief outline it follows that pulse radiolysis is now a very versatile instrument for studying free–radical reactions. It is important to note that this technique is not restricted to the study of free–radical intermediates, but often short–lived diamagnetic intermediates can be rapidly generated and their subsequent fast reactions can be measured. A few of the many examples are described in Refs. [13–19].

3. Radiolysis of water

The majority of the radiation–chemical studies is carried out in dilute aqueous solution. Hence, practically all the radiation energy is absorbed by the solvent and the water radicals generated by the absorption of the ionizing radiation (reaction 1) interact with the solute. With the help of the pulse radiolysis technique rate constants of the water radicals with a large number of organic and inorganic substrates have been determined. They are compiled in Ref. [20]. If not stated otherwise rate constants given here are taken from this compilation.

$$H_2O \xrightarrow[\text{radiation}]{\text{ionizing}} {}^{\cdot}OH,\ e^-_{aq},\ H^{\cdot},\ H^+,\ H_2,\ H_2O_2 \qquad (1)$$

In the past, radiation chemists have developed a whole set of experimental conditions by which the primary water radicals can be transformed into other radicals or scavenged specifically by additives. For example, saturating the solution with N_2O (solubility 10^{-2} mol dm^{-3} at 20 °C) will convert the solvated electron into an OH radical (reaction 2, k_2 = 9.8 x 10^9 dm^3 mol^{-1} s^{-1}), resulting in a rather clean OH radical source (90% ·OH, 10% H·).

Usually N_2O is rather inert against free–radical attack. However it does react with reducing radicals such as the formate radical $CO_2^{\cdot -}$, albeit with a low rate constant ($k(CO_2^{\cdot -} + N_2O)$ = 1600 dm^3 mol^{-1} s^{-1}) [21]. Although this reaction does not play a role in pulse radiolytic investigation, it must be taken into

account when experiments are carried out at the low dose rates of ^{60}Co–γ–radiolysis.

$$N_2O + e^-_{aq} \longrightarrow {}^{\cdot}OH + N_2 + OH^- \quad (2)$$

In acid solution the solvated electron is converted into an H atom (reaction 3, k_3 = 2 x 10^{10} dm^3 mol^{-1} s^{-1}). If a given H–atom reaction is to be investigated at neutral pH use can be made by the fact that phosphate buffer as well can convert the solvated electron into an H–atom, albeit with a considerably lower rate constant (reaction 4, k_4 = 1.9 x 10^7 dm^3 mol^{-1} s^{-1}). The remaining ·OH radicals can be eliminated by adding *t*–butanol (reaction 5, k_5 = 5 x 10^8 dm^3 mol^{-1} s^{-1}). The resulting *t*–butanol–derived radical is usually rather inert, at least at the time–scale of most pulse radiolysis experiments. The radicals which then attack the solute are only H atoms, since the H atom reacts only slowly with *t*–butanol (k(H· + *t*–butanol) = 1.7 x 10^5 dm^3 mol^{-1} s^{-1}).

$$e^-_{aq} + H^+ \longrightarrow H^{\cdot} \quad (3)$$

$$e^-_{aq} + H_2PO_4^- \longrightarrow H^{\cdot} + HPO_4^{2-} \quad (4)$$

$$^{\cdot}OH + (CH_3)_3COH \longrightarrow H_2O + {}^{\cdot}CH_2C(CH_3)_2OH \quad (5)$$

In basic solution the H–atom is converted into a solvated electron (equilibrium 6; pK_a(H·) = 9.6) and the OH radical into $O^{\cdot -}$ (equilibrium 7, pK_a(·OH) = 11.9). Thus, in N_2O–saturated strongly alkaline solutions all the water radicals are converted into $O^{\cdot -}$.

$$H^{\cdot} \rightleftharpoons e^-_{aq} + H^+ \quad (6)$$

$$^{\cdot}OH \rightleftharpoons O^{\cdot -} + H^+ \quad (7)$$

With organic substrates OH radicals and H atoms add to C–C double bonds and abstract carbon–bound H atoms, whereby addition is preferred over H–abstraction. The $O^{\cdot -}$ radical, however, has only a low tendency to add to C–C double bonds but its H–abstractive power is close to that of the OH radical. In systems which present both kinds of reactive center, such as phenylacetate ions [22] or nucleosides [23] this can bring about a considerable change in the product distribution on going from e.g. pH 10 (OH radical reactions) to e.g. pH 14 ($O^{\cdot -}$ radical reactions).

Often the reduction potential of a given solute is high enough to be reduced not only by the solvated electron or the H atom, but quite readily also by other reducing radicals such as $CO_2^{\cdot -}$ ($E(CO_2^{\cdot -}/CO_2)$ = – 2000 mV) [24] which can

be generated from formate ion according to reactions 8 and 9, k_8 = 3.2 x 10^9 dm^3 mol^{-1} s^{-1}, k_9 = 2.1 x 10^8 dm^3 mol^{-1} s^{-1}).

$$\cdot OH + HCO_2^- \longrightarrow H_2O + CO_2^{\cdot -} \quad (8)$$
$$H^\cdot + HCO_2^- \longrightarrow H_2 + CO_2^{\cdot -} \quad (9)$$

However, it must be taken into account that the formate radical has also oxidizing properties ($E(CO_2^{\cdot -}, H^+/HCO_2^-)$ = + 1070 mV) [24].

The OH radical and the H atom can be used to produce a number of radicals for further reaction with other solutes, e.g. for the investigation of methyl radicals reactions 10 or 11 can be used.

$$\cdot OH + CH_4 \longrightarrow H_2O + \cdot CH_3 \quad (10)$$
$$\cdot OH + (CH_3)_2SO \longrightarrow \cdot CH_3 + CH_3SO_2H \quad (11)$$

For kinetic studies (pulse radiolysis) the DMSO reaction [25, 26] might be of advantage, but for product studies the methane system is certainly cleaner. However, due to the low solubility of methane in water, it requires working at elevated pressures [27].

The water radicals may also be converted into some inorganic radicals which have some very interesting properties. For example, the OH radical in its reaction with the bromide ion is eventually converted into $Br_2^{\cdot -}$ (overall reaction 12) and the $SO_4^{\cdot -}$ radical may be generated by the reaction of $S_2O_8^{2-}$ with the solvated electron and the H atom (reaction 13, k_{13} = 1.2 x 10^{10} dm^3 mol^{-1} s^{-1} (2.5 x 10^7 dm^3 mol^{-1} s^{-1})).

$$2\ Br^- + \cdot OH \longrightarrow Br_2^{\cdot -} + OH^- \quad (12)$$
$$S_2O_8^{2-} + e_{aq}^- \ (H^\cdot) \longrightarrow SO_4^{\cdot -} + SO_4^{2-} \ (HSO_4^-) \quad (13)$$

These radicals can be used as one-electron oxidants, $SO_4^{\cdot -}$ being the stronger oxidant (E = 2430 mV) than $Br_2^{\cdot -}$ (E = 1660 mV) [24]. They thus allow to produce radical cations of various substrates (see below).

Molecular oxygen reacts rapidly with the solvated electron (reaction 12, k_{12} = 1.9 x 10^{10} dm^3 mol^{-1} s^{-1}) and the H-atom (reaction 13; k_{13} = 2.1 x 10^{10} dm^3 mol^{-1} s^{-1}). The resulting radicals are in equilibrium ($pK_a(HO_2^\cdot)$ = 4.8) [28].

$$O_2 + e_{aq}^- \longrightarrow O_2^{\cdot -} \quad (12)$$
$$O_2 + H^\cdot \longrightarrow HO_2^\cdot \quad (13)$$

The OH radical does not react with O_2, however its basic form, $O^{\cdot -}$, readily yields the ozonide ion (reaction 14, k_{14} = 3.6 x 10^9 dm^3 mol^{-1} s^{-1}).

$$O_2 + O^{\cdot -} \longrightarrow O_3^{\cdot -} \qquad (14)$$

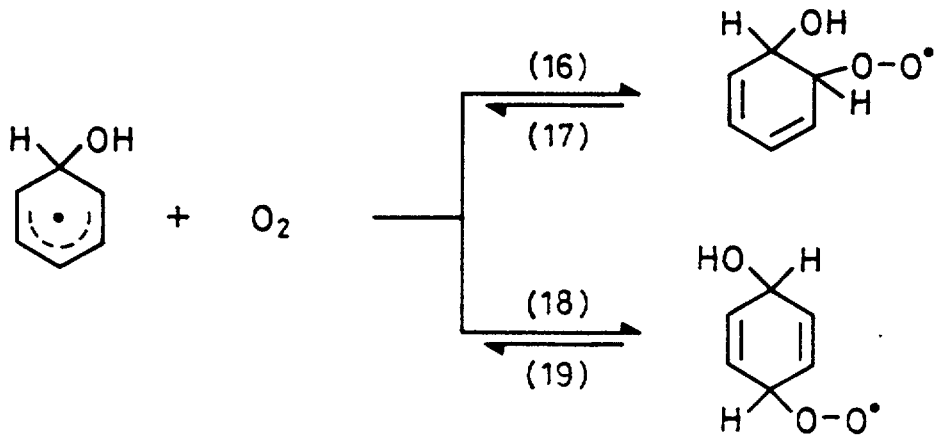
Organic radicals usually react readily with O_2 [29] and a most interesting peroxyl radical chemistry ensues.

4. Peroxyl radicals

In a natural environment oxygen is abundant not only in the gas phase, but equilibrium concentrations in aqueous solutions and liquid organic matter are also quite high ($\geq$ 2.5 x 10^{-4} mol dm^{-3}). Most carbon–centered radicals react with oxygen at close to diffusion–controlled rates ($k_{15} \approx 2 \times 10^9$ dm^3 mol^{-1} s^{-1}) yielding the corresponding peroxyl radicals (reaction 15) [29].

$$R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot} \qquad (15)$$

In the majority of the systems investigated so far the reaction is practically irreversible at room–temperature, but from product studies it has been concluded that in the case of the pentadienyl radicals derived from polyunsaturated fatty acids oxygen addition must be reversible (for references see Ref. [3]). Using the pulse–radiolysis technique this has also been shown to occur with hydroxycyclohexadienylperoxyl radicals ($^{\cdot}$OH/benzene/O_2) (reactions 16–19) [30].



It is expected that in the near future more systems will be found where such a reversibility plays a role. In this context it is interesting to note that some substituted hydroxycyclohexadienyl radicals do not react significantly with oxygen on the pulse radiolysis timescale [31]. The reason for this may be a very rapid release of oxygen from a peroxyl radical intermediate, reflecting a weak

$R–O_2^{\cdot}$ bond. Reversible reactions are also observed for the reaction of thiyl radicals with oxygen ($RS^{\cdot} + O_2 \rightleftarrows RSOO^{\cdot}$; see below).

The peroxyl radical function is a strongly electron–withdrawing group. Hence, the peroxyl radicals derived from acetic acid are much more acidic (pK_a = 2.1, equilibrium 20/21) than acetic acid itself (pK_a = 4.8). From these data the Taft σ^* constant of the $^{\cdot}OOCH_2$–group has been calculated at 1.55 [32].

$$^{\cdot}OOCH_2CO_2H \rightleftarrows {}^{\cdot}OOCH_2CO_2^- + H^+ \qquad (20/21)$$

Peroxyl radicals are fairly strong oxidants [33]. The most powerful one known is the acetylperoxyl radical [34].

In a few cases the peroxyl radicals are not observed as intermediates (although they are likely intermediates) because they release rapidly $O_2^{\cdot -}$ (e.g. overall reactions 22 and 23) [35, 36].

$$CO_2^{\cdot -} + O_2 \longrightarrow CO_2 + O_2^{\cdot -} \qquad (22)$$

$$(CH_3)_2NCH_2^{\cdot} + O_2 \longrightarrow (CH_3)_2N{=}CH_2^+ + O_2^{\cdot -} \qquad (23)$$

On the other hand, when the substrate is not such a strong electron donor, the rate of $O_2^{\cdot -}$ release can be measured by pulse radiolysis on the microsecond timescale. A case in point is the tertiary peroxyl radical derived from acetaldehyde dimethyl acetal (reaction 24, $k_{24} = 6.5 \times 10^4\ s^{-1}$) [37].

$$CH_3C(OCH_3)_2O_2^{\cdot} \longrightarrow CH_3C(OCH_3)_2^+ + O_2^{\cdot -} \qquad (24)$$

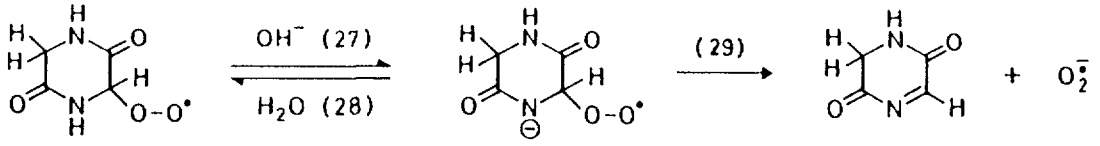
It has been known for a long time that peroxyl radicals derived from primary and secondary alcohols eliminate $HO_2^{\cdot}$, and from their basic form, $O_2^{\cdot -}$ (reactions 25 and 26) [38].

$$R_2C(OH)O_2^{\cdot} \longrightarrow HO_2^{\cdot} + R_2C{=}O \qquad (25)$$

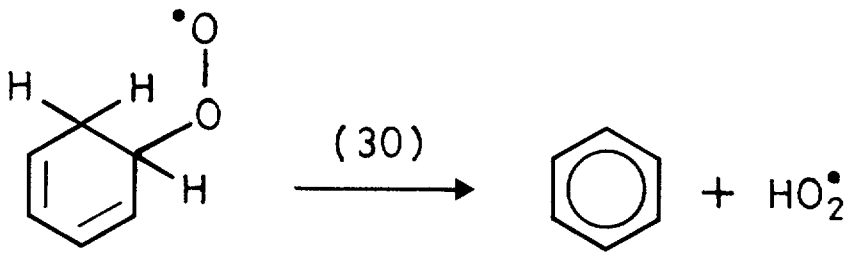
$$R_2C(O^-)O_2^{\cdot} \longrightarrow O_2^{\cdot -} + R_2C{=}O \qquad (26)$$

These reactions largely govern the peroxyl radical chemistry of carbohydrates (e.g. Refs. [39, 40]).

Peptide peroxyl radicals when deprotonated at nitrogen also eliminate $O_2^{\cdot -}$ in a reaction similar to reaction 26 (reaction 29). A rapid elimination of $HO_2^{\cdot}$ from the neutral radical (*cf.* reaction 25) is not observed. Hence, it is possible to determine the pK_a value of such peptide peroxyl radicals (equilibrium 27/28). The observed value agrees with the one calculated on the basis of the Taft σ^* constant of the peroxyl radical function mentioned above.



Another type of $HO_2^{\cdot}$–elimination is observed with the cyclohexadienyl–peroxyl radicals (reaction 30 $k_{30} \geq 8 \times 10^5\ s^{-1}$).



With the hydroxycyclohexadienyl radical it has been shown that only one isomer, the peroxyl radical with a 1,3–cyclohexadienyl structure, but not the other isomer (1,4–cyclohexadienyl structure) eliminates $HO_2^{\cdot}$ [41].

In competition with the $HO_2^{\cdot}/O_2^{\cdot -}$ elimination, or in cases where such elimination reactions cannot take place, several bimolecular decay routes may be followed. There is good evidence (at low temperatures and in organic solvents) that tetroxides are intermediates (*cf.* reaction 31) [42]. Major decay routes are represented by the Russell mechanism (reaction 33) [43], the elimination of hydrogen peroxide (reaction 34) [44, 45], and the formation of oxyl radicals (reaction 36). In this context it is interesting to note that in aqueous solutions oxyl radicals undergo a rapid 1,3–H–shift (reaction 38, *cf.* Ref. [46] and references cited therein) in competition to their well–known fragmentation (reaction 40). There are some data which suggest that such fragmentation reactions may well proceed without the intermediacy of oxyl radicals (reaction 35) [47]. The dimerization of two oxyl radicals yielding the peroxide (reaction 41) usually does not play an important role (*cf.* Ref. [27])

$$2\ R_2CHO_2^{\cdot} \rightleftharpoons R_2CHO_4CHR_2 \qquad (31/32)$$

$$R_2CHO_4CHR_2 \longrightarrow R_2CO + O_2 + R_2CHOH \qquad (33)$$

$$R_2CHO_4CHR_2 \longrightarrow 2\ R_2CO + H_2O_2 \qquad (34)$$

$$R_2CHO_4CHR_2 \longrightarrow 2\ RHCO + O_2 + 2\ R^{\cdot} \qquad (35)$$

$$R_2CHO_4CHR_2 \longrightarrow 2\ R_2CHO^{\cdot} + O_2 \qquad (36)$$

$$2\ R_2CHO^{\cdot} \longrightarrow R_2CO + R_2CHOH \qquad (37)$$

$$R_2CHO^{\cdot} \longrightarrow {}^{\cdot}C(OH)R_2 \qquad (38)$$

$${}^{\cdot}C(OH)R_2 + O_2 \longrightarrow R_2CO + HO_2^{\cdot} \qquad (39)$$

$$R_2CHO^{\cdot} \longrightarrow RCHO + R^{\cdot} \qquad (40)$$

$$2\ R_2CHO^{\cdot} \longrightarrow R_2HCO_2CHR_2 \qquad (41)$$

It is obvious from the aforementioned chemistry of the peroxyl radicals that a large number of peroxyl radicals undergo $HO_2^{\cdot}/O_2^{\cdot-}$ elimination, but due to reactions 38 and 39 some $HO_2^{\cdot}/O_2^{\cdot-}$ is also formed in the course of their bimolecular decay.

Because of its slow bimolecular decay, the radical $O_2^{\cdot-}$ may rise to relatively high steady–state concentrations. The deleterious effects of oxygen to the living cell ("oxygen stress" [48]) is thought to be largely due to the formation of the superoxide radical anion, $O_2^{\cdot-}$ and its subsequent reactions with transition metal ions (e.g. Refs. [49–53]). For this reason most cells have enzymes, the superoxide dismutases, which cope with this radical [54].

Otherwise the $O_2^{\cdot-}$ radical is a rather inactive species. It does not undergo H–abstraction reactions (e.g. Ref. [55]), and in the case of thiolate oxidation a rather complex mechanism appears to operate [56]. There are a few exceptions from the rule that $O_2^{\cdot-}$ is rather inert. It is readily scavenged by antioxidants such as pyrogallol and n–propyl gallate. The reaction is again not by H–abstraction but rather initiated by an addition to the ring [57]. This type of reaction also seems to prevail in the $O_2^{\cdot-}$ induced decarboxylation of 1,3–dihydroxymandeleic acid [58], the 3,4–mandeloquinone being a likely intermediate (*cf.* Ref. [59]). A surprising chain reaction leading to carbon dioxide and oxalic monoperacid is induced when $O_2^{\cdot-}$ adds to the ketomalonate ion [60]. These are a few recent results from our laboratory, and we are convinced that in the near future more reactions of the $O_2^{\cdot-}$ radical will be observed. Often they cannot be followed by pulse radiolysis because the rate constants are low, but due to its long lifetime (slow self–termination), such reactions are easily noticed at low dose rates.

Further expansion of our knowledge of peroxyl free–radical chemistry is obviously warranted. In radiobiological studies it has been shown that cells are considerably more radiosensitive in the presence of oxygen than in its absence [3]. This must of course be due to the intervention of peroxyl radicals. Hence in the near future much research will be directed toward a better understanding of peroxyl radical reactions, not only on low–molecular–weight material (as has mainly been done so far) but also on biologically important polymers such as DNA, proteins and polymeric carbohydrates. Pulse radiolysis with low–angle–laser–light–scattering will be one of the techniques to study the kinetics of strand breakage (and crosslinking) in such biopolymer systems (e.g. Ref. [61]). The superoxide radical can be conveniently produced using radiation techniques (e.g. *via* reaction 22), and its reactions with biomolecules studied. Up to the present time, only its very fast reactions ($k > 10^6$ dm^3 mol^{-1} s^{-1}) have been investigated as slower reactions cannot be followed easily by pulse radiolysis. However,

because of the long intrinsic lifetime of $O_2^{\cdot -}$ (with respect to bimolecular decay [28]) reactions with rate constants < 10^6 dm^3 mol^{-1} s^{-1} may be of biological importance.

5. Nucleic acids

As radiation biology and radiotherapy continue their progress, and as more refined methods become available to measure the relevant radiation–induced changes at the molecular level, detailed models of radiation–induced cell killing, mutagenesis and transformation (carcinogenesis) continue to be developed. There is still a considerable knowledge gap to be bridged between the biological effects and the radiation–chemical events preceding them. Our present knowledge in this area has been reviewed recently [3]. Thus, it will be sufficient to point out the most important aspects and the frontier of research in this field.

There is general agreement that the main target regarding these biological endpoints is the cellular DNA [3]. In the living cell, the causes of radiation–induced DNA damage are twofold. There is the *direct effect* where the energy of the ionizing radiation is absorbed by the DNA molecule itself, and the *indirect effect* where the ionizing radiation is absorbed by the aqueous surroundings of the DNA. The latter produces the water radicals ·OH, H· and e_{aq}^-. Their reactions have been studied by investigating dilute aqueous solutions of DNA or its constituents. In the past, considerable effort has been put into a better understanding of the free–radical chemistry of the nucleic acid constituents, in particular the pyrimidines uracil, thymine and cytosine, and model systems of the sugar–phosphate moiety induced by the water radicals. The corresponding reactions of the purines adenine and guanine [62, 63] are less well understood.

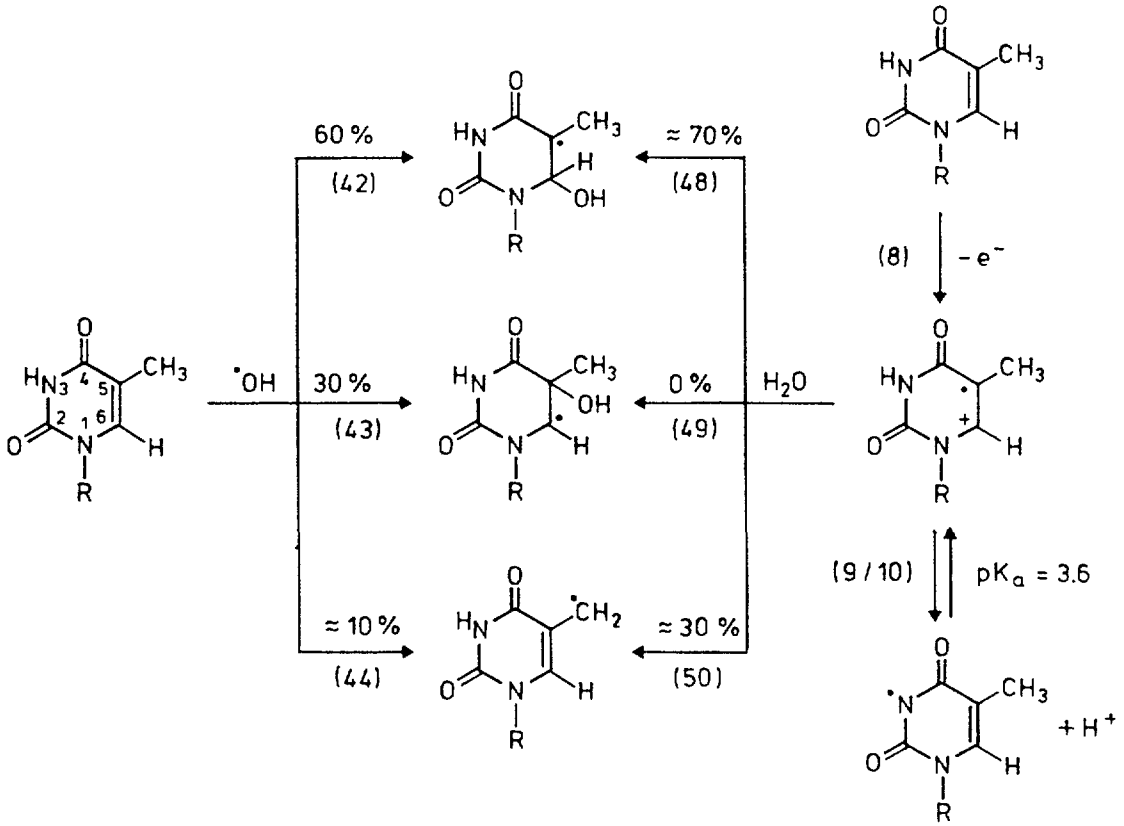
Some important aspects of nucleic acid free–radical chemistry are given here briefly (for details see Ref. [3, 63, 64]). The solvated electron reacts with diffusion–controlled rate constants with the nucleobases. In uracil and thymine the electron adducts are in equilibrium with their O–protonated forms whose pK_a values are close to 7 [65]. The radical anions and their O–protonated forms have reducing properties, e.g. in their reaction with oxygen $O_2^{\cdot -}$ is formed [66], oran electron can be transferred to 5–bromouracil [64, 67]. In competition with a rapid protonation at the heteroatom there is a much slower protonation at C–6. The resulting radical no longer has reducing properties and is therefore no longer capable of undergoing the above–mentioned reactions. The radical anions of cytosine and adenine are both very rapidly protonated by water ($t_{½}$ in the nanosecond time range) [68–71]. In the case of adenosine the rapid protonation by water clearly occurs first at the heteroatom ($A^{\cdot -} \rightarrow ANH^{\cdot}$; $pK_a(ANH^{\cdot}) = 12.1$

[63]); OH^-–induced deprotonation being the reverse reaction. Out of this equilibrium, the comparatively slow protonation at carbon ensues ($A^{\cdot -} \rightarrow ACH^{\cdot}$).

An interesting question is the transfer of an electron from a nucleobase radical anion to another nucleobase. The direction of this electron transfer will be governed by the electron affinities of the nucleobases. However, if these electron affinities are not very different from one another, quasi–equilibria will become established, wherefrom the (irreversible) protonation reactions at carbon may lead to a fixation of the damage. Some experiments with aview of elucidating this question have already been performed [64].

In its reaction with the the nucleobases, the OH radical mainly adds to the double bond, while H abstraction reactions, e.g. from the methyl group of thymine or the sugar moiety in the case of the nucleosides/nucleotides are of minor importance (≤ 10%, *cf.* reactions 42–44). Except for the the case of purines (for a recent review see Ref. [63]), very little additional information on the OH radical reactions has been accumulated with low–molecular–weight model systems since the extensive review given in Ref. [3], and details will not be repeated here. However, detection of such damage in irradiated DNA has made considerable progress [72–86], although the available data clearly indicate that only a fraction of the DNA damage inflicted by OH radicals can be accounted for by the existing techniques, and it is obvious that these will have to be improved in the near future. A potential tool is the use of repair enzymes which excise damaged sections from the DNA strand [87]; these might be analyzed and identified.

The *direct effect* is quite difficult to investigate separately from the *indirect effect*. Important intermediates resulting from the direct effect must, of course, be radical cations produced upon ionizations. Radiation–chemical techniques allow to generate powerful oxidants such as $SO_4^{\cdot -}$ in aqueous solution to produce such intermediates (e.g. Ref. [88]), and it is hoped that our present limited knowledge in this area will improve considerably in the near future. As an example one may take the reaction of thymidine with $SO_4^{\cdot -}$ [89]. Although an $SO_4^{\cdot -}$ adduct radical may be formed, it is too short–lived to be observable at the microsecond time scale. The first observed product is the radical cation which has a life–time of only about 2 μs. It may deprotonate at N(3) (reaction 46; pK_a(radical cation) = 3.6) but also reacts with water yielding the C(6)OH, C(5)yl radical (reaction 48), and deprotonates at the C^5–methyl group (reaction 50). The C(5)OH, C(6)yl radical which is a prominent product in the case of OH radical attack (reaction 43), is not formed in the decay of the radical cation. Due to the low pK_a value of the radical cation the N(3)–centered radical has a certain life–time at neutral pH. This raises the question whether it may play a role in DNA radiation chemistry by undergoing reactions not discovered so far. Here again, product studies are urgently needed.



An important aspect in radiation biology is the interaction of thiols (mainly glutathione which in cells can reach levels close to 10^{-2} mol dm^{-3}) with DNA radicals which can "repair" some of its radiation damage by H–donation or electron transfer (from the thiolate [90–93]). This process is termed *chemical repair* (as compared to an enzymatic repair by the enzymatic repair system) (see also the section on sulfur compounds). In model systems, e.g. with polynucleotides, this reaction has been investigated in some detail [94–98] and also extended to DNA (*cf.* Ref. [99] and references cited therein).

6. Proteins

Pulse radiolysis has yielded a large body of information on the free–radical reactions of amino acids, small peptides, and proteins [3]. Also, considerable knowledge has accumulated on radiation–induced impairment of enzyme function and a lot has been learned about enzyme functioning [3]. Here is another example where radiation chemistry has proved to be able to transcend the boundaries of merely studying the effects of radiation, and to contribute to our general knowledge of chemistry and biochemistry where other techniques may fail. However, on the whole, the radiation chemistry of proteins is not yet well understood, despite the fact that we already have a considerable knowledge concerning the radiation chemistry of aqueous solutions of amino acids and the nature of radicals formed in crystalline amino acids.

In most of the studies done so far the radiolysis of proteins has been investigated in aqueous solutions where the indirect effect predominates, i.e. radiation damage is caused by the water radicals, ·OH, e^-_{aq} and H. Only a fraction of the amino acid subunits of a larger protein are exposed to the aqueous environment, and it is these amino acid subunits which are most likely attacked. As a consequence, radiation damage must be rather surfaced–biased. In addition, we have to take into account that the sulfur–containing and aromatic amino acids are more reactive towards the water radicals than the aliphatic amino acids. A good deal of the low reactivity of the free aliphatic amino acids is due to the inactivating effects of the $-NH_3^+$ (and $-CO_2^-$) residues. In the protein these groups largely disappear, most of them now contributing to the peptide linkages. This enhances drastically the reactivity of the water radicals with such subunits (as compared to the amino acid zwitterions). This may be exemplified by comparing the reactions of ·OH and e^-_{aq} with glycine zwitterion and its dimer, glycine anhydride: k(·OH + glycine) = 1.7 x 10^7 dm^3 mol^{-1} s^{-1}; k(·OH + glycine anhydride) = 1.2 x 10^9 dm^3 mol^{-1} s^{-1}; $k(e^-_{aq}$ + glycine) = 8.9 x 10^6 dm^3 mol^{-1} s^{-1}; $k(e^-_{aq}$ + glycine anhydride) = 1.7 x 10^9 dm^3 mol^{-1} s^{-1}.

Table I compiles data given for the small protein papain which contains only 212 amino acid subunits. About one half of them are exposed, only 16% of these exposed amino acids are of the more reactive aromatic and sulfur–containing ones. In pulse radiolytic investigations of proteins and peptides, the contribution of the aliphatic amino acids is usually neglected because the signals from the intermediates derived from the aromatic and sulfur–containing amino acids predominate. In future research more attention will have to be paid to this contribution.

Table 1. Aromatic and sulfur–containing amino acids in papain [100].

Amino acid	Content	Exposed
Cysteine	1	1
Histidine	2	2
Cystine	3	2
Phenylalanine	4	2
Tryptophan	5	2
Tyrosine	19	13
Peptide units	212	106

The recent observation of radical transfer processes in sarcosine anhydride [101] raises anew the question as to what extent such reactions occur also in the proteins. Radical transfer processes within the protein have often been invoked to explain the radiation–induced inactivation of enzymes. Pulse radiolytically, transformations of radicals derived from aromatic and sulfur–containing amino acid residues [102] are more readily observable due to distinct absorption spectra. This is why we know so much more about these radical transfer processes. Most notable is the formation of tyrosin–derived phenoxyl radicals (TyrO·); e.g. by the tryptophan radical (Trp·, reaction 51) [103–108].

$$Trp^{\cdot} + TyrOH \longrightarrow TrpH + TyrO^{\cdot} \qquad (51)$$

In the presence of oxygen most of the protein–derived radicals are converted into the corresponding peroxyl radicals. In the course of their decay the protein skeleton may be broken or compounds may be formed which disintegrate subsequently. As a consequence, smaller fragments are observed after irradiation. The breaks do not occur at random but there are preferred sites [109]. The position of these sensitive sites and the mechanism of strand breakage are as yet unknown.

In this context it is interesting to note that peptide–peroxyl radicals eliminate (after deprotonation at nitrogen) $O_2^{\cdot -}$ radicals as has been studied in some detail in the case of glycine anhydride and alanine anhydride (reactions 27–29). Although at neutral pH the OH^-–concentration is very low, i.e. the formation of the peptide peroxyl radical anion (reaction 27) is slow, the overall reaction (reactions 27–29) is sufficiently fast to compete against the bimolecular decay of the peptide peroxyl radicals, at least at the low dose rates of ^{60}Co–γ–radiolysis ($\leq$ 1 Gy s^{-1}).

Concerning the OH–adduct radicals of phenylalanine their behaviour is very similar to their prototypes, the hydroxycyclohexadienyl radicals (derived from benzene + ·OH). It has been shown in the peroxyl radical section that in the presence of oxygen such radicals are in equilibrium with their corresponding peroxyl radicals. These hydroxycyclohexadienyl peroxyl radicals are capable of eliminating $HO_2^{\cdot}$ yielding o–, m– and p–tyrosine, but also undergo considerable fragmentation of the carbon skeleton of the benzene ring. In N_2O/O_2–saturated solutions G(o–Try) = 1.0, G(m–Tyr) = 0.9 and G(p–Tyr) = 1.0 x 10^{-7} mol J^{-1}, i.e. only about one half of the OH adduct radicals are converted into the three phenols [110].

It has been mentioned above that in the biological systems a considerable part of the damage must be caused by the energy absorbed by the proteins

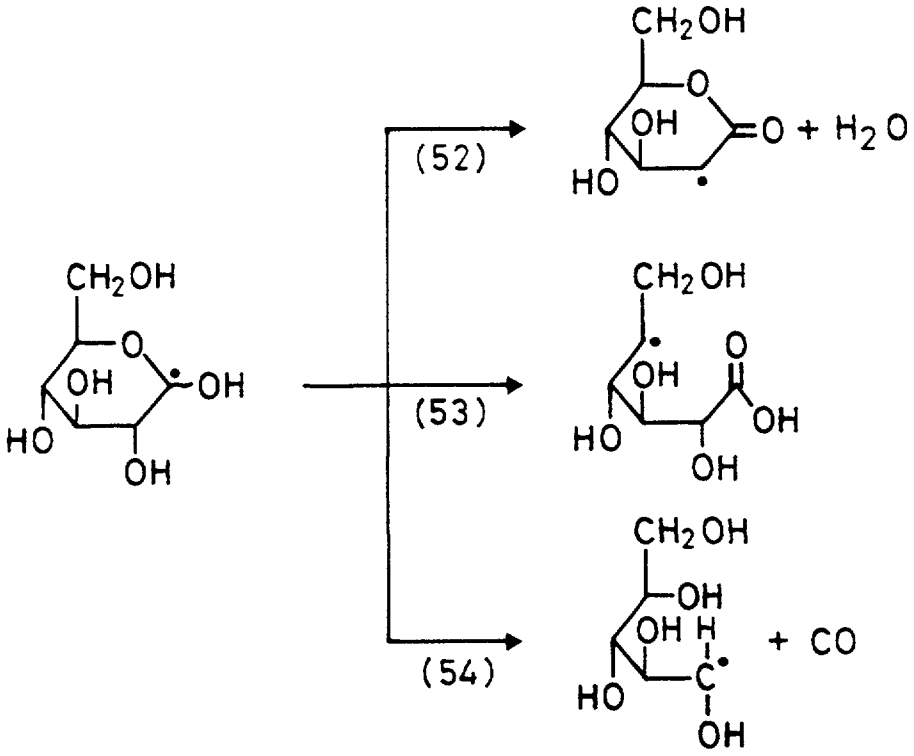
themselves and not only by the surrounding water. This direct effect has not yet been studied in detail. In the case of the aromatic amino acids it should be possible to mimic the effect by reacting $SO_4^{\cdot -}$ radicals (and other inorganic radicals) with these substrates. A number of pulse radiolysis data are available, but product studies have been carried out so far only for phenylalanine. Again, o–, m– and p–tyrosine are among the products, but also considerable carbon dioxide formation is observed. This is explained by an intramolecular electron transfer from the carboxylate group of Phe to the radical cation site in the ring, followed by decarboxylation of the carboxyl radical thus formed.

In the foreground of present–day research are questions of electron transport through proteins, e.g. in photosynthesis. It is hoped that radiation techniques will be able to make a significant contribution.

A more applied aspect is food irradiation and concomitant changes in the protein component. The determination of the dose applied to a given foodstuff is still not fully established [111]. Although some methods based on the chemical change of some protein constituents such as phenylalanine are in course of being developed [112, 113], more fundamental research is certainly needed for a better understanding of the underlying primary processes (*cf.* Ref. [110]).

7. Carbohydrates

In the past, the radiation chemistry of carbohydrates has found considerable attention and our present knowledge of the free–radical chemistry of this class of compounds is fairly well advanced [114] [3, 115], both in solutions and in the solid state where in selected cases some interesting free–radical chain reactions were observed (*cf.* Ref. [116–119]). In the low–molecular–weight carbohydrates, water elimination reactions (e.g. reaction 52) and rearrangement reactions (e.g. reaction 53) dominate the radiation chemistry of aqueous solutions in the absence of oxygen. In the presence of oxygen, the $HO_2^{\cdot}$–elimination reaction (e.g. reaction 25; for the kinetics see Ref. [40]) is the most abundant type of reaction (e.g. in D–glucose [39]).



In contrast to the low–molecular–weight carbohydrates studied so far, considerably less is known about the biologically more important carbohydrate polymers such as hyaluronic acid [61], and it is evident that more will have to be learned about the radiation–induced degradation of such biopolymers. In this context it is worth noting that DNA in a sense is a polymer carbohydrate, and that radical attack at its sugar moiety leads to important lesions, such as strand breakage and base release.

8. Lipids

Because of their low solubility in water and their tendency to form micelles and liposomes, lipids and their subunits, the fatty acids, are difficult to study in aqueous solutions without the presence of such aggregates and *vice versa* [3]. On the other hand, the formation of aggregates is a typical behaviour of these systems and changes the free–radical chemistry, radical transfer and (in the presence of oxygen) peroxidation [120–122].

In the polyunsaturated fatty acids the biallylic H atoms are the most loosely bound and hence are abstracted, even by fairly poor H–abstractors such as thiyl radicals (k(RS$^{\cdot}$ + linoleic acid) = 10^6 dm^3 mol^{-1} s^{-1}) [123].

The need for developing sensitive probes to monitor the dose given to irradiated food [111] will cause a renewed interest also in studying details of the direct effects of ionizing radiation on lipids (fats [124, 125]), especially the formation of cyclobutanones [126].

9. Sulphur compounds

In the past, sulfur compounds have attracted radiation chemists since these compounds display a most interesting free–radical chemistry and radiation techniques such as pulse radiolysis have contributed a lot to the high level of our present knowledge [3, 127]. There remain, however, many open questions and it is expected that radiation chemistry will continue to be leading in this field of research.

A few typical reactions should be mentioned here. Many of the intermediates involve three–electron S–S bonds [127].

With thiols, OH radicals readily form thiyl radicals (reaction 55, $k_{55} \geq 10^{10}$ dm^3 mol^{-1} s^{-1}).

$$RSH + {}^{\cdot}OH \longrightarrow RS^{\cdot} + H_2O \qquad (55)$$

In the presence of thiolate ions the thiyl radicals rapidly form $RSSR^{\cdot -}$ radicals (equilibrium 56/57; $k_{56} \approx 10^9$ dm^3 mol^{-1} s^{-1}, $k_{57} \approx 10^6$ s^{-1}) [128–131]. The same species is formed when the solvated electron reacts with disulfides (reaction 58, $k_{58} \approx 10^{10}$ dm^3 mol^{-1} s^{-1}).

$$RS^{\cdot} + RS^- \rightleftharpoons RSSR^{\cdot -} \qquad (56/57)$$

$$RSSR + e^-_{aq} \longrightarrow RSSR^{\cdot -} \qquad (58)$$

In acid solutions such complexes fall apart (reactions 59–61), because the thiol itself does not as readily complex with the thiyl radical as does the thiolate ion.

$$RSSR^{\cdot -} + H^+ \rightleftharpoons RSSR(H^{\cdot}) \longrightarrow RSH + RS^{\cdot} \qquad (59–61)$$

In alkyl dithiol (cyclic disulphide) systems there is some evidence for the $RSSR(H^{\cdot})$ intermediate [130, 132]. However, these systems are far from being well–understood.

Besides these radical anions sulfur is capable of forming a number of radical cations such as $R_2S^{\cdot +}$, $R_2SSR_2^{\cdot +}$, $RSSR^{\cdot +}$. Since the $R_2S^{\cdot +}$ species is formed from sulfides (overall reaction 62, $k_{62} \approx 10^9$ dm^3 mol^{-1} s^{-1}), the dimeric radical cation is always in equilibrium with the monomeric radical cation (equilibrium 63/64) [133, 134].

$$R_2S + {}^{\cdot}OH \longrightarrow R_2S^{\cdot +} + OH^- \qquad (62)$$

$$R_2S^{\cdot +} + R_2S \longleftrightarrow R_2SSR_2^{\cdot +} \qquad (63/64)$$

In its reaction with the disulfide the OH radical also eventually can lead to the formation of a radical cation (overall reaction 65) [135].

$$RSSR + {}^{\cdot}OH \longrightarrow RSSR^{\cdot+} + OH^{-} \qquad (65)$$

In radiation biology thiyl radicals are bound to play a very important role. The thiol glutathione can reach levels as high as 10^{-2} mol dm^{-3}, and many carbon–centered radicals react quite rapidly ($k \approx 10^7 - 10^8$ dm^3 mol^{-1} s^{-1}) with thiols by H abstraction (reaction 66). It is interesting to note that some oxidizing radicals (good electron acceptors) do not, or at least only very slowly, react with thiols, but they do react quite fast with the thiolate ion (e.g. reaction 68, $k_{68} \approx 10^8$ dm^{-3} mol^{-1} s^{-1}) ([136], *cf.* also references given above).

$$R^{\cdot} + RSH \rightleftharpoons RH + RS^{\cdot} \qquad (66/67)$$

$$RS^{-} + CHOCH_2^{\cdot} \longrightarrow RS^{\cdot} + CH_2{=}CH(O^{-}) \qquad (68)$$

Thus, in cells a large number of the radicals which are primarily formed by the absorption of the ionizing radiation will eventually be converted into thiyl radicals. However, reaction 66 is also reversible (reaction 67). In the case of ethers [137] and secondary alcohols [138] the reverse reaction occurs with rate constants of about 10^4 dm^3 mol^{-1} s^{-1}, in polyunsaturated fatty acid with even 10^6 dm^{-3} mol^{-1} s^{-1} [123]. On the other hand allyl radicals (and hence certainly also pentadienyl radicals) barely abstract an H atom from the thiol [139, 140], i.e. reaction 66 is very slow in this case.

Thiyl radicals react very rapidly with oxygen (reaction 69, $k_{69} \approx 10^9$ dm^3 mol^{-1} s^{-1}), however this reaction is reversible (reaction 70, $k_{70} \approx 10^5 - 10^6$ dm^3 mol^{-1} s^{-1}) [141, 142].

$$RS^{\cdot} + O_2 \rightleftharpoons RSOO^{\cdot} \qquad (69/70)$$

A most interesting reaction sequence follows, which is not yet fully elucidated. ESR data suggest that reaction 71 may occur [143–145].

$$RSOO^{\cdot} + RSH \longrightarrow RSO^{\cdot} + RSOH \qquad (71)$$

There is also the chance of an intramolecular rearrangement (reaction 72), because the $RSO_2^{\cdot}$ radical has a much lower energy. Theoretical calculation show that there must be a considerable barrier for this rearrangement [146]. In accordance with this $k_{72} \leq 10^4$ s^{-1} has tentatively been estimated as an upper limit [142].

$$RSOO^{\cdot} \longrightarrow RSO_2^{\cdot} \quad (72)$$

Disulfide, sulfonic acid, and sulfuric acid are major products in the decay of the peroxyl radical derived from 2–mercaptoethanol [142]. This, especially the formation of sulfuric acid, shows that the reaction mechanism must indeed be complex. It is apparent that solving the problem of $RSOO^{\cdot}$ chemistry will be a major goal for radiation chemists working in this field. This knowledge may help to understand the interesting sensitizing effect of oxygen in cellular systems when exposed to ionizing radiation.

10. Unusual oxidation states of non–metals other than sulfur

Compared to sulfur, very few studies have been made with compounds containing other hetero atoms. It might be certainly worth–while to have a closer look at tervalent phosphorous and carbon–bound phosphorous and similar systems (e.g. Se–, Te– and I–compounds) to enhance our knowledge in heteroatom free–radical chemistry.

11. Transition metal ions

In chemistry there is an important trend to explore the usefulness of catalytic reactions, many of which are mediated by transition metal ions.

In fact, radiation–chemical techniques allow to study in detail the chemistry of transition metal ions in unusual valence states [11, 147]. They can be reached by either oxidation or reduction of stable oxidation states, by OH radicals or the solvated electron (or other reducing agents such as $CO_2^{\cdot -}$).

A case in point is the formation of Fe(IV) by the oxidation of Fe(III) with the OH radical (reaction 73), or the reduction of Fe(VI) by $CO_2^{\cdot -}$ which yields Fe(V) (reaction 74) [148].

$$Fe(III) + {}^{\cdot}OH \longrightarrow Fe(IV) + OH^- \quad (73)$$

$$Fe(VI) + CO_2^{\cdot -} \longrightarrow Fe(V) + CO_2 \quad (74)$$

Such hypervalent states are thought to play an important role in many metallo–enzymes such as P450, and radiation techniques may well provide the key for a better understanding of the functioning of these metallo–enzymes.

The Cu–catalysed chain oxidation of methanol by hydrogen peroxide apparent does not proceed, as has been believed for a long time, by a free OH radical as an intermediate, but rather by a Cu(III) species (reactions 75–78) [149, 150].

$$Cu(I) + H_2O_2 \longrightarrow Cu(III) \quad (75)$$

$$Cu(III) + CH_3OH \longrightarrow Cu(II) + \cdot CH_2OH + H^+ \quad (76)$$

$$Cu(II) + \cdot CH_2OH \longrightarrow Cu(I) + CH_2O + H^+ \quad (77)$$

$$Cu(III) + Cu(I) \longrightarrow 2\ Cu(II) \quad (78)$$

In addition, radiation techniques provide an excellent tool for producing small metal clusters, the chemistry of which is very different from that of the bulk metal. It is expected that this area of research (e.g. Refs. [151, 152]) will be expanding and will yield results of far–reaching importance.

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APPLIED RADIATION CHEMISTRY RESEARCH

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Abstract

Radiation research has provided the fundamental data on which most of the applications of radiation are based. New lines of research have led to an increase in the scope and versatility of existing radiation processing as well as to the development of new techniques. The contribution made by radiation research to the selected areas will be presented.

In the nuclear power industry, coolant water is subjected to irradiation at high temperatures. Here radiation chemistry research is being used to obtain kinetic and thermodynamic information to permit accurate computer modelling of the complex series of reactions occurring. These models can then be used to optimise operating conditions. One of the oldest applications of radiation is in radiotherapy of cancer. Now radiation research is assisting in the construction of new radiosensitising drugs. Radiation sterilising plants for medical equipment are now in operation world-wide. In this field research continues to provide improved 'radiation properties' of the materials used for packaging and construction. Radiation is also being applied to sterilize human and animal tissue, and research in this field has led to the establishment of Human Tissue Banks. Food quality can be improved by irradiation. Legislation requires the availability of a test for irradiated food, and research is underway to provide such a test. Atmospheric pollution is now a matter of major public concern. Atmospheric chemistry is complex but radiation chemistry experiments are now providing valuable indications of certain of the processes involved. All uses of radiation require accurate dosimetry. Now research is providing better and more convenient dosimeters. Finally the widespread occurrence of free radicals in chemical and biochemical systems is now recognised. Radiation chemistry research is the method of choice for investigating the properties of these reactive species.

1. INTRODUCTION

Ionising radiations, as the name implies, interact with matter to produce electrons and ions. Further reactions of these species give rise to the formation of free radicals which are usually highly reactive and are eventually converted to diamagnetic products. Living organisms are susceptible to ionising radiations which has led to their use in medicine, for the sterilization of medical products and in the radiotherapy of cancer. Polymerisation reactions can also be initiated by free radicals, produced by irradiation. Many free radical mediated processes occur in biology and chemistry. Irradiation provides the ideal method for generating and studying the properties of these free radicals. Radiation chemistry research is the template on which many of the applications of radiation are forged. This paper illustrates how applied radiation research is now leading to new areas of understanding. Those fields specifically covered by other contributors to this compilation namely polymerisation and polymer grafting are not included. Of necessity, we have had to be selective in our illustrations of the rapid progress in this subject.

2. CURRENT AREAS OF APPLIED RESEARCH

2.1 Nuclear Reactor Chemistry

Various components of nuclear power plants are subjected to ionising radiation at high dose rates and for prolonged times. One such component is the coolant, most commonly water. The absorption of radiation by water results in the formation of water derived radicals and products. These species react with each other, with any solutes present and with the fabric of the container. If optimum running conditions, including plant durability and the safety of maintenance staff, are to be achieved, the chemistry occurring in these systems must be understood.

$$H_2O \xrightarrow[\text{radiation}]{\text{ionising}} \cdot OH,\ H\cdot,\ e^-_{aq},\ H^+,\ H_2O_2,\ H_2 \qquad (1)$$

$$\cdot OH + H_2O_2 \longrightarrow H_2O + HO_2\cdot \qquad (2)$$

$$HO_2 \rightleftharpoons H^+ + O_2\cdot^- \qquad (3)$$

$$HO_2\cdot + HO_2 \longrightarrow H_2O_2 + O_2 \qquad (4)$$

$$HO_2\cdot + O_2\cdot^- \xrightarrow{H^+} H_2O_2 + O_2 \qquad (5)$$

$$H\cdot + O_2 \longrightarrow HO_2\cdot \qquad (6)$$

It has been well established e.g.[1,2] that the exposure of water to ionising radiation gives rise to the species shown in equation (1). Subsequent reactions e.g. (2 - 6) lead to the appearance of species such as $HO_2/O_2\cdot^-$ and O_2. For high LET radiation oxygen appears to be produced within the tracks by other reactions. One suggested possibility is the bimolecular decay of excited water molecules (reaction 7)[3].

$$2H_2O^* \longrightarrow 2H_2 + O_2 \qquad (7)$$

It is now clear that as many as 80 reactions [4] must be considered when attempting to understand the chemistry within nuclear reactors. The only hope of modelling such complex systems is computer simulation. However, in order to set up these models, kinetic and thermodynamic data for all of the reactions must be known. The task of providing this information falls to the radiation chemist.

2.1.1 High temperature effects

Nuclear reactors operate at high temperatures and the temperature of the water during radiolysis is in the region of 300°C. The operating temperature of a Boiling Water Reactor, for example, is 286°C [5]. Consequently, in order to be useful, experimental data applicable to these elevated temperatures must be obtained which, of course, poses major practical problems. Free radicals are usually very reactive species and in solution only exist for short times even at ambient temperatures, so that in order to study their properties directly 'fast reaction techniques' must be employed. The technique of pulse radiolysis is now routinely used for these types of study and a number of

TABLE I

Reactions whose experimentally determined rate constants give reasonably linear Arrhenius plots

Reaction	Temp.Range /°C	k at 20°C[a] /$dm^3mol^{-1}s^{-1}$	Activation[a] Energy/$kJmol^{-1}$	Reference
(5) $HO_2\cdot + HO_2\cdot$	20 - 300	8.4×10^5	20.6	[9]
(8) $H_2O_2 + \cdot OH$	14 - 160	2.7×10^7	14	[5]
(9) $H_2 + \cdot OH$	20 - 230	3.4×10^7	19	[7]
(10) $HCO_3^- + \cdot OH$	20 - 200	8.5×10^6	21.2	[10]
(11) $CO_3^{2-} + \cdot OH$	20 - 200	3.6×10^8	23.6	[10]
(12) $Cu^{2+} + \cdot OH$	20 - 220	3.8×10^8	13.3	[6]
(13) $Fe^{2+} + \cdot OH$	20 - 220	4.5×10^8	9.0	[6]
(14) $H^+ + e^-aq$	20 - 200	2.3×10^{10}	13.8	[4]
(15) $O_2 + e^-aq$[b]	20 - 200	1.7×10^{10}	13.5	[4]

[a] Errors $\pm$ 15% or less

[b] Calculated values show plot curves at > 200°C [4]

establishments throughout the world are equipped with this important major tool. Although many pulse radiolysis facilities are equipped to perform experiments up to 100°C, very few are adapted for use at higher temperatures. In fact most of the work on high temperature aqueous solutions is being performed at the Riso National Laboratory, Denmark, Cookeridge Radiation Research Centre, UK, and at the University of Tokyo, Japan.

The temperature (T) dependencies of the rate constants (k) for a number of reactions have been investigated up to temperatures in excess of 100°C and in most cases to around 200°C [4-10]. For many of the reactions Arrhenius plots (lnk against 1/T) were found to be linear (see Table I). This is, however, by no means the case for all reactions investigated as illustrated in Figure 1 for the dimerisation of hydroxyl radicals (reaction 16) [4].

$$\cdot OH + \cdot OH \text{ -----> } H_2O_2 \qquad (16)$$

$$\phi NO_2 + e^-aq \text{ -----> } \phi NO_2^{\cdot -} \qquad (17)$$

$$\cdot OH + HCO_2^- \text{ -----> } CO_2^{\cdot -} + H_2O \qquad (18)$$

Similarly, Arrhenius plots for reactions (6), (17) (ϕ = benzyl) and (18) are also distinctly curved [4]. Two basic processes are involved in chemical reactions.

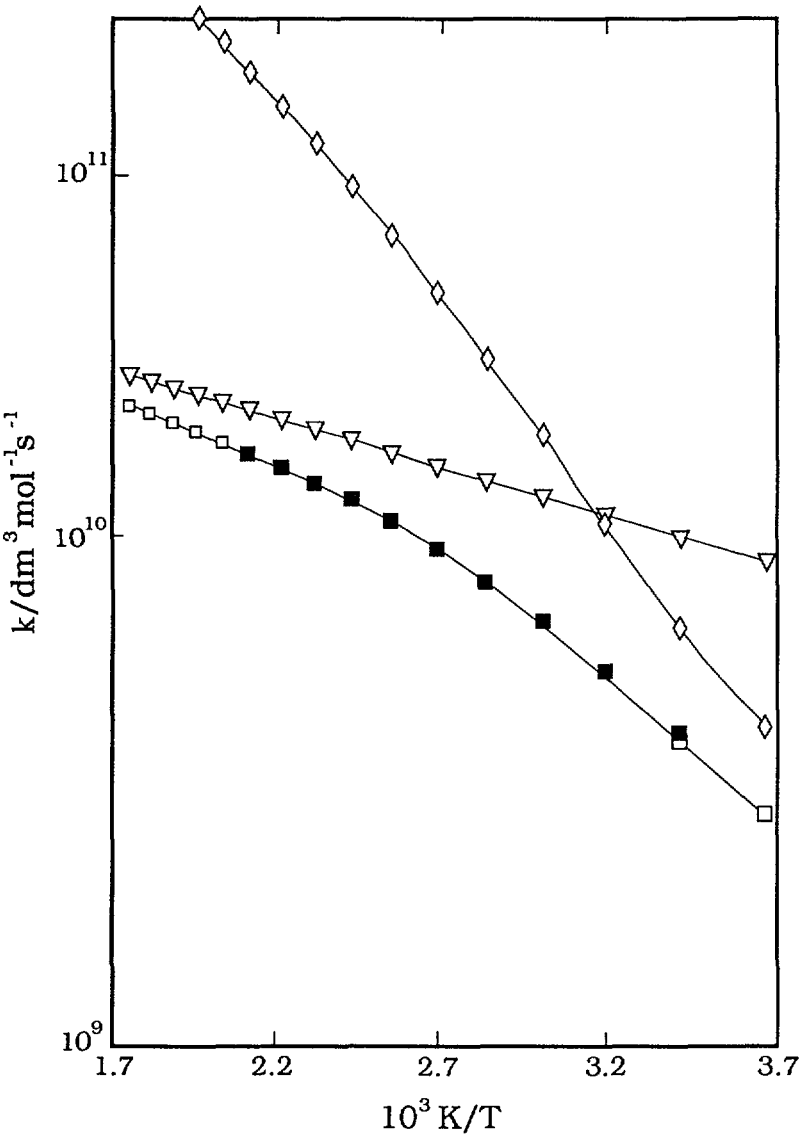

Figure 1. Rate constants for the dimerisation of OH radicals: k_{obs} ,■; k_{diff}, ◊; k_{calc} , □. Taken with permission from [4]

The first is diffusion of the reactants together resulting in a 'collison'; the second is passage of the 'collison complex' over the activation barrier with the formation of products. Buxton and his collaborators have applied equation (19) which relates the observed rate constant (k_{obs}) to the diffusion rate constant (k_{diff}) and the reaction rate constant (k_{react}), to their rate constant / temperature data for reactions (6) (14) (15) (16) and (18) as well as to several other reactions [4].

$$1/k_{obs} = 1/k_{diff.} + 1/k_{react} \qquad (19)$$

k_{diff} is the rate constant assuming every encounter between reactants leads to products, allowing for the neccessity for the reaction complex to be in a singlet state for product formation. k_{diff} can be calculated from the Smoluchowski equation using literature and/or estimated values for the relevant diffusion coefficients and reaction radii. When charged reactants are involved, the value of k_{diff} must be corrected to allow for electrostatic repulsion or attraction. This can be achieved using the Debye factor which is readily calculable. k_{react} is by definition equal to $A\exp(E_{act}/RT)$ i.e. the

Arrhenius equation, where A is the pre-exponential factor and E_{act} is the activation energy. The best fit of calculated values for the rate constant, using calculated k_{diff} and varying E_{act} and k_{react} at 25°C, to experimental values was made based on equation (19). When the reactants are ionic, corrections to both k_{diff} and k_{react} were performed to allow for the kinetic salt effect [4]. Included in Figure 1 are k_{diff} and k_{react} and the calculated rate constant k_{calc} for the dimerisation of OH radicals. It is evident that at low temperatures the reaction is mainly diffusion controlled whereas at high temperatures it becomes mainly reactivity controlled. There is good agreement between calculated and measured values across the whole temperature range which enables some confidence to be placed in values calculated outside the range of measurement [11]. When an encounter occurs between two radicals, products will only be formed from an encounter complex in the electronic singlet state. If the spin-lattice relaxation time is much longer than the lifetime of the complex, and since three triplet states exist for each singlet state, only 25% of encounters will lead to a reaction. Most radicals behave in this manner and k_{diff} must be corrected by multiplying by 0.25. If this is not done, good fits of calculated to measured data cannot be achieved [4]. For OH radical dimerisation, however, a fit could only be obtained if no such correction was applied to k_{diff}. The implication here is that ·OH has a short spin lattice relaxation time so that spin reorientation occurs within the lifetime of the collision complex and all encounters lead to products. Estimates of the spin lattice relaxation time of the OH radical indeed indicated it to be very short [12]. To obtain a good correlation between measured and calculated results for a number of reactions of e^-_{aq}, Buxton and his collaborators found that the temperature dependence of the diffusion coefficient of e^-_{aq} had to be similar to that of water rather than those of H^+ or OH^-. It would, therefore, appear that e^-_{aq} does not diffuse by a conduction-type mechanism although the magnitude of its diffusion coefficient suggests the involvement of additional processes such as tunnelling.

Other reactions of the solvated electron have been found to have linear Arrhenius plots in the low temperature range (20-130°C) but at higher temperatures the observed rate constants were found to decrease with increasing temperature. Reactions exhibiting this type of behaviour are the dimerisation of e^-_{aq} [8] and the reactions of e^-_{aq} with nitrous oxide, nitrite and nitrate ions [4]. The formation of an intermediate (dielectron) was put forward to account for this observation for e^-_{aq} dimerisation, with the intermediate dissociating to yield either two e^-_{aq} or products (reaction 20). Similar schemes might operate in the other systems, but more research is required to elucidate precisely what processes are occurring.

$$e^-_{aq} + e^-_{aq} \rightleftharpoons (e^-_{aq})_2 \text{ -----> } H_2 + 2OH^- \qquad (20)$$

The rate constant for reaction of $O_2\cdot^-$ with $HO_2\cdot$ (reaction 5) was found to increase more rapidly with increasing temperature in the higher temperature range (> 130°C) than in the lower temperature range (20-70°C) [9]. This has been explained in terms of there being a change in the reaction mechanism as the temperature is raised, with the reversible formation of O_4^{2-} from the dimerisation of $O_2\cdot^-$ possibly becoming important at high temperatures [9].

Dissociation constants are temperature dependent and in seeking to model processes occurring at elevated temperatures, changes in the values of dissociation constants for the various species must be considered. The ionic dissociation constant (K_w) of water itself increases with increasing temperature. Studies have been made on the temperature dependencies of the acid dissociation constants of $HO_2\cdot$ (reaction 3) and ·OH (reaction 21) both of which are present in irradiated water.

$$\cdot OH \rightleftharpoons H^+ + O^{\cdot -} \quad (21)$$

Reaction (21) has been investigated by utilising the much lower reactivity of $O^{\cdot -}$ towards CO_3^{2-} compared to ·OH [10]. From a knowledge of the temperature dependence of the reaction of ·OH with CO_3^{2-} and HCO_3^-, the pH of the solution and the dependence of the HCO_3^-/CO_3^{2-} equilibrium constant on temperature, determinations of the rate constant for the formation of $CO_3^{\cdot -}$ (·OH + CO_3^{2-}) at varying temperatures enables the temperature dependence of the acid dissociation constant (K_a) of ·OH to be evaluated. A Van't Hoff plot ($\ln K_a$ against reciprocal temperature ($^oK^{-1}$)) was curved (20-200°C), indicating that the enthalpy for dissociation of ·OH decreases, as for water, with increasing temperature [10]. In contrast, the complementary reaction (reaction (22)) with OH^- was found to yield a linear Van't Hoff plot (ΔH = 15.4 kJ mol^{-1})[10] in agreement with earlier work performed over a much lower temperature range [13]. At 20°C the pK_a for ·OH is 11.8 falling to 10.1 at 200°C [10].

$$O^- + H_2O \rightleftharpoons OH + OH^- \quad (22)$$

$HO_2^{\cdot}$ and $O_2^{\cdot -}$ have different optical spectra which provides the basis of a relatively simple method for determining the acid dissociation constant of $HO_2^{\cdot}$ (reaction 3) by measuring the combined absorbance of $HO_2^{\cdot}/O_2^{\cdot -}$ as a function of pH. In pulse radiolysis measurements the absorbance due to any species is given by G x ε, where G is the yield of the species and ε is its extinction coefficient. Thus if ε is known G can be calculated from the absorbance or if G is known ε can be calculated. There are no large changes in the shape of the $HO_2^{\cdot}$ and $O_2^{\cdot -}$ spectra in the temperature range 20-175°C [10] and 20-300°C [9]. However, the value of G x ε for $O_2^{\cdot -}$ increased with increasing temperature [9,10]. Some discrepancies appear with respect to G x ε for $HO_2^{\cdot}$ the value is reported to remain constant (pH 1.9, 240 and 260 nm, 20-175°C) by one group [10] but to increase with increasing temperature (pH 2, 224 nm, 20-300°C) by another group [9]. The question as to whether the yields of the water derived radicals change with the temperature of radiolysis is most important and will be considered later. Assuming an increase in the yields of both $HO_2^{\cdot}$ and $O_2^{\cdot -}$ with increasing temperature, the dissociation constant of $HO_2^{\cdot}$ was found to be temperature independent in the range 20-175°C [10]. A similar conclusion came from work at lower temperatures (3-75°C) [13]. Over a wider temperature range (20-300°C), it was found that although the acid dissociation constant for $HO_2^{\cdot}$ was temperature independent below 100°C, at temperatures above 150°C it showed a marked increase in value (4.8 at 20°C, 6.15 at 285°C) [9]. Corrections were made for increases in G x ε with increasing temperature for $HO_2^{\cdot}$ and $O_2^{\cdot -}$ assuming ε to be temperature dependent.

The values of the radiolytic yields of all radiolytic products are a prime requisite in setting up models to simulate coolant water radiolysis. In dilute aqueous solutions at ambient temperature (20°C) the yields of the various radicals and species produced by radiation are now well accepted [1,2]. Some controversy still remains as to the effect of temperature on radiolytic yields [14]. One view is that only slight increases in G values occur as the temperature rises, another is that G values increase appreciably. Steady-state experiments, in which the yield of fluoride ions from the reaction of e^-_{aq} with SF_6 was used to evaluate $G(e^-_{aq})$ were interpreted as showing a substantial increase (78%) in the radiolytic yield of e^-_{aq} on going from 23 to 300°C [15]. A smaller 40% rise in $G(e^-_{aq})$ with increasing temperature (20-250°C) was reported based on the results of pulse radiolysis work [16]. The view that G values increase on increasing the radiolysis temperature has

received strong support from pulse radiolysis measurements in which the yield of reduced methyl viologen (spectrum temperature independent 20-300°C) [17] which directly reflects the total radical yield, rose by 25% over the 20-200°C range [18]. Radiolytic yields based on H_2 measurements for H_2 and e^-_{aq}, have recently been shown to increase (up to 50%) on increasing the temperature during γ-radiolysis [19].

Radiation research provides information fundamental to setting up computer simulations to represent the complex series of reactions going on in nuclear reactor coolant water. The effect of temperature on these reactions, and indeed on the state of protonation of some of the reactants cannot always be predicted on the basis of low temperature studies. Measurements at elevated temperatures are, therefore, necessary, such measurements have not only provided data for simulations but have also lead to advances in our understanding of the associated physical chemistry.

2.1.2 Radiation induced corrosion and dissolution of metal oxides

Corrosion is a general problem in systems where water is in contact with iron or steel, a problem which increases in severity at higher temperatures. Radiolysis increases the rate of corrosion by a factor of 10-20 fold [20], so that nuclear reactor cooling systems are particularly liable to corrosion. Additional problems arise due to the deposition of corrosion products (metal oxide particles) close to the reactor core. As well as adversely altering local heat-transfer characteristics, their exposure to high energy radiations results in nuclear transformations and induced radioactivity. Subsequent deposition at sites remote from the core causes a serious hazard for maintenance personnel.

Metal corrosion is an oxidative process whereby metal atoms are converted to metal ions. Water radiolysis produces both oxidative (·OH, HO_2·/O_2·$^-$) and reductive (H·, e^-_{aq}) species. It has been suggested that HO_2·/O_2·$^-$ participate in the radiation induced enhancement of corrosion although detailed mechanisms are not yet elucidated [21]. In neutral and alkaline solutions, iron ions hydroxylate and form aggregates. In the presence of oxygen $Fe(II)_{aq}$ is oxidised to $Fe(III)_{aq}$. The radiolysis of neutral solutions of a number of metal ions in their reduced states leads to the formation of colloidal oxides in the higher oxidation state, the initial reaction being with ·OH (for details see [22] and references therein). Thus thermal and radiation induced reactions lead to metal oxides which are present as colloids or precipitates.

The formation of these metal oxides involves radiolytically generated oxidative species. However, reduction of colloidal metal oxides results in their dissolution [23,24]. The isopropanol radical reacts with colloidal haematite (a form of Fe_2O_3) at diffusion controlled rates at pH < 3.2 and results in dissolution of the Fe(III) as Fe(II) [23]. At pH 9.2 no dissolution was observed. For colloidal particles of magnetite (Fe_3O_4), isopropanol radicals also react at diffusion-controlled rates at pH 2 (no reaction occurring at pH 7). However in terms of Fe (II) release, the efficiency falls rapidly with increasing dose from 100% to 25% [23,24]. This has been interpreted as being due the initial presence of sufficient Fe(III) sites at the colloidal surface for every encounter to lead to a reaction, whereas at later stages fewer Fe(III) sites remain available [24]. Experiments using radiolytically generated Fe(II)-EDTA as reductant demonstrated that Fe(II) formed in colloidal magnetite by reduction of Fe(III) dissolved more rapidly than the Fe(II) originally present (magnetite has the composition $Fe(II)(Fe(III))_2O_4$). The reactivity and redox potentials of colloids are very dependent on the surface charge, which itself is pH-

dependent. Studies were made at pH 7 on a number of colloidal ferrites using reduced methyl viologen, MV+ (methyl viologen = 1, 1' dimethyl 4, 4' bipyridinium) which is positively charged and is readily produced radiolytically.

Reductive dissolution of colloidal magnetite, cobolt ferrite, and nickel ferrite by MV+ was observed at pH 7 [24]. The rate determining step appears to be the release of Fe(II) from the colloid by reduction of Fe(III). When colloidal magnetite was added to a solution of MV+, the Fe^{2+} released was only equivalent to 25% of the disappearance of MV+. It was suggested that a build-up of Fe(II) from reduced Fe(III) at the colloid surface acts as a microelectrode (negatively charged) and reduces MV+. In competition with MV+ reduction is release of Fe(II) [24]. Electron microscope measurements revealed that reductive dissolution of magnetite proceeds at localised sites on the colloid with the appearance of large pits in the surface. In contrast cobalt ferrite colloid dissolved uniformly throughout the lattice [24].

Despite the intrinsic complexities involved in corrosion in nuclear reactors valuable insights into the processes can now be gained by the careful application of radiation chemistry.

2.1.3 Other processes

The accidental release of radioactive iodine from malfunctioning nuclear reactors is a major concern. Radiation chemistry studies are being carried out to develop models which can be used to find ways of minimising iodine release. Following an accident, iodine would be present in various forms in the solid, aqueous and gaseous phases. In the aqueous phase alone some 29 reactions involving iodine species, water radicals and oxygen [25] have been identified. More work on the effects of temperature and other solutes is still needed.

2.2 Radiobiology

Ionising radiation causes mutation, transformation and reproductive death on interaction with living cells. Right from the early days of what is now known as radiation biology or radiobiology, it was realised that there were large differences in the radiation sensitivities of different cell types [26]. The mechanisms of radiation induced cell damage and the exploitation of this effect in radiation cancer therapy have, as befits such an important subject, received a tremendous research input. Radiation chemistry research has made and continues to make significant contributions to the progress being achieved in radiobiology. In this short review it is impossible to cover the entire field and only some aspects will be discussed. More information is given in the references [1,26-31].

Radiotherapy continues to be the most widely used treatment for cancer. Under ideal circumstances any treatment should destroy carcinogenic cells whilst leaving the surrounding normal cells intact. One way of attempting to approach this situation would be to selectively sensitise tumour cells to radiation killing. An alternative solution being actively pursued is to attach radionuclides emitting short range radiations to tumour specific antibodies [32]. Mammalian cells are most sensitive to radiation induced killing during that phase in their growth cycle when their DNA is replicating i.e. S-phase [33]. Cancer cells frequently but by no means always, replicate more rapidly

than normal cells, thus increasing their radiosensitivity. This provides the basis for much of the success of radiation therapy. It has long been known that oxygen is a cell radiosensitiser [34], and in fact it is the best yet discovered. The vascular system in tumours is poor, so that often the centre of large tumours is anoxic and in this region the cells die. Between this region and the outer well-oxygenated region is a hypoxic region. Here the tumour cells remain viable whereas their radiosensitivity is much reduced due to their lower O_2 content [27]. In this way the natural situation is the reverse of ideal, in that the hypoxic tumour cells are less sensitive to radiation killing than the surrounding normal cells. Strenuous endeavours have been made to find radiosensitisers capable of 'mimicing' oxygen and increasing the radiosensitivity of hypoxic cells. Nitro-aromatic compounds seem to offer some prospect of success and have been extensively studied [35,36].

A measure of the effectiveness of a hypoxic radiosensitiser is the concentration of sensitiser required to increase by a specific amount, the fraction of cells killed by a given radiation dose. For several series of nitro compounds it was shown that the sensitising effectiveness, measured as the concentration of sensitiser needed to increase cell killing by 1.6, was linearly related to the one electron reduction potential (see Figure 2) [35]. Since for a given basic ring structure the redox potentials of a series of compounds are linearly related to the Hammett constants of the substituents, it is possible to construct radiosensitisers with predictable sensitising efficiencies. Radiation chemistry played a prime role in defining these relationships by facilitating the determination of the requisite one electron redox potentials. Indeed when short-lived (i.e. highly reactive) species are produced following one electron oxidation or reduction, pulse radiolysis provides the only satisfactory technique for these measurements. Many such redox potentials have now been measured and compiled [37]. The principles of the measurement are described elsewhere [1,36,38,39]. As can be seen from Figure 2, the one electron redox potential of oxygen (-0.155V) is greater than those of the nitro

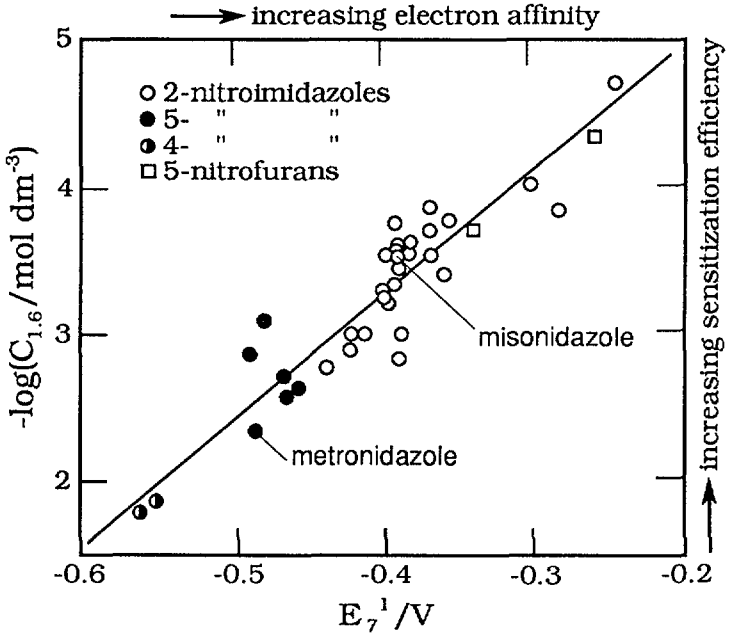

Figure 2. Relationship between redox potential and cellular radiation sensitising efficiency of various nitro compounds. Taken with permission from [35]

compounds which means that the one electron reduced nitro compounds i.e. the radical anions may be oxidised by oxygen (reaction 23).

$$RNO_2^{\cdot -} + O_2 \text{ ----> } RNO_2 + O_2^{\cdot -} \quad (23)$$

In cells, nitro compounds undergo enzymic reduction and under anaerobic conditions cell death occurs. Oxygen however, almost completely prevents this effect. The explanation is thought to be that the decay of the nitroanion leads to lethal damage but when the anion is converted to $O_2^{\cdot -}$ (reaction 23) this damage no longer occurs [36]. It is, of course, this anoxic toxicity which led to the use of nitro compounds as drugs to destroy anaerobic bacteria. The detailed reactions between nitro-aromatics and various radicals including DNA radicals, has shown that adducts may be formed as intermediates. The extent to which such intermediates are produced and their rate of heterolysis can be understood on the basis of the respective structures of the radical and the nitro-aromatic [40].

Investigations are now being undertaken into the possibility of combining the hypoxic cell radiosensitising property and the anaerobic toxicity of nitro compounds in cancer treatment by inducing total tumour hypoxia immediately following irradiation [41].

As well as sensitisation, cellular radioprotection must be considered, both in radiotherapy and in attempting to reduce the drastic effects of radiation in the event of nuclear accidents. Experiments have shown that thiols are largely responsible for intracellular chemical radiation protection [1, 42].

The detailed examination of the radiation induced reactions responsible for damaging specific biological systems makes possible the development and testing of prospective methods for sensitisation and protection.

2.3 Medical Products and Biomaterials

From an energetic standpoint ionising radiations are extremely efficient in killing living organisms. A good example of this is provided in the case of humans where a whole body dose of ca. 4Gy is lethal. The same amount of energy supplied as heat would raise the victims body temperature by around one thousandth of a degree centigrade and would pass unnoticed. Lower life forms are generally more resistant to radiation. Nevertheless it has now been known for many years that irradiation can reduce microbial contamination in an article to fewer than 10^{-6} microorganisms, the medically acceptable level of sterility assurance [43]. There are a number of advantages in using ionising radiation for sterilisation; processing occurs at ambient temperature, allowing the treatment of thermolabile materials; samples can be sealed prior to treatment and remain sealed until their subsequent use; radiation plants can be designed to have high volume throughputs, and in contrast to gas sterilisation, there is no evidence of harmful residues remaining in the sterilised material. On safety, reliability and economic considerations radiation sterilisation compares most favourably with other techniques [44]. The IAEA has been actively involved in promoting research and in organising international meetings on radiation sterilisation and radiation treatment plants are now operating successfully throughout the world. Although there is general unanimity regarding the ability of radiation treatment to achieve accepted sterility assurance levels, there is some slight disagreement as to the size of the minimum dose required [45]. The IAEA Guidelines on this subject identify the parameters which enable satisfactory dose levels to be set

and suitable process control procedures to be achieved. The main thrust of radiation research in this area is associated with the effects of irradiation on the structure and composition of the material undergoing radiation sterilisation. Other important applications of radiation research in medicine such as polymer grafting and drug encapsulation are the subject of other articles in this publication and are not discussed here.

2.3.1 Packaging materials

The maintenance of sterility following radiation treatment necessitates sealing the treated material in microorganism-proof packages. Clearly the packing material must itself be sterile and the packaging of irradiated products must be performed aseptically. By irradiating pre-sealed packages both the product and its packaging are simultaneously sterilised, while the packaging process, which take place before sterilisation, can be performed under normal working conditions. Of course, this mode of operation subjects the packaging material to irradiation, and it is important that the effects of this exposure are known. Plastics are the most widely used packaging material, as well as being used in making many medical products. The properties of medical plastics are regulated by national legislatures (Pharmacopoeia) and cover toxicological and mechanical aspects, amongst others [44,46]. Many investigations have been undertaken to determine radiation induced alterations in plastics. These range from discolouration to changes in mechanical properties [46]. In some polymers, e.g. poly(dimethylsiloxane) radiation induced crosslinking is much greater than radiation induced chain scission, whereas in others, e.g. cellulose, the reverse is true [47]. In the presence of oxygen polymer peroxyl radicals are formed and these can enter into chain reactions resulting in high yields of hydroperoxides which are thermally unstable and give rise to long-term post-irradiation peroxidative damage. As a consequence it is important to ensure adequate supplies of antioxidants are incorporated in the plastic. Dose rates affect the yields of products, so that often substantial differences can be detected between electron beam and gamma-irradiated material subjected to the same dose. As an example, lower yields of volatile oxidative degradation products are reported to be formed in polythene by electron beam as opposed to gamma-irradiation [48]. A list of plastics deemed suitable for radiation, along with the names and addresses of their manufacturers is given in reference [44]. Polyethylene and polypropylene are widely employed in packaging. Radiation has been shown to reduce the levels of phenolic antioxidants in these plastics. In this regard there were no significant differences between gamma and electron beam irradiation [49]. The extent of reduction in antioxidant concentration was dependent on the identities of the antioxidant and the polyolefine. The radiation induced changes in polyvinyl chloride (PVC), a commonly used plastic in medical applications, are very dependent on the particular formulation followed during manufacture. It has been reported recently that PVC's can be produced which, even after radiation doses of 50 kGy, are not discoloured and fulfil all legislative requirements for their use in medicine [46].

Detailed investigations of the radiation chemistry of polymers are hindered by difficulties in quantifying and identifying products which remain bound in the polymer chain. One way of avoiding this difficulty is to apply results obtained from monomer irradiation to the polymer. Such data is, of course, extremely useful in assisting the elucidation of processes operating in the irradiated polymer. However, some caution must be exercised. A good illustration of this is polyacrylic acid and polymethacrylic acid which, on the basis of the behaviour of their respective monomers, might be expected to have similar radiation properties. This is not so since irradiation degrades (i.e. reduces the

molecular weight of polymer molecules) polyacrylic acid but causes crosslinking (increase in molecular weight) in polymethacrylic acid [50]. Electron spin resonance (ESR) studies have enabled the intermediate radical species to be identified and it is proposed that the much higher susceptibility of the radical produced by decarboxylation to β-cleavage (i.e. chain scission) in the polymethacrylic acid system accounts for the observed difference. This radical is not directly observed by ESR, but its fragmentation product can be identified.

The initial event in irradiated systems is ionisation with the formation of an electron and a positive ion. The reactions and properties of these species in organic liquids have been reviewed elsewhere [51]. In solid polymeric systems these ionic species are the primary products of irradiation and their reactions dictate the final outcome. Microwaves are attenuated by the presence of conducting species and this fact has been used in conjunction with pulse radiolysis to monitor the kinetics of the reactions of radiation induced ions in non-polar media [52]. This technique has been applied to organic polymers in the solid state and for teflon (polytetrafluoroethylene) it appears that the radiolytically produced electron is able to move from one fluorine atom to the next with no rupture of the C-F bond [53]. There seems to be considerable scope for further research into the processes taking place in these materials.

Polymer properties can be altered significantly by radiation, and this modification can be either detrimental or beneficial depending on the use to which the material is to be put. In designing new materials, radiation has an important part to play, and it is only through radiation research that our understanding can increase sufficiently to enable full exploitation of this field.

2.3.2 Biomaterials

The term biomaterial here is used for natural or synthetic materials which are used in contact with living tissue or biological fluids. Included in this category are pharmaceuticals, cosmetics, bandages, sutures as well as implements such as syringes and tubing. All of these types of products must be sterile prior to use and radiation treatment offers an excellent means of ensuring the necessary degree of sterility. Before employing radiation to sterilise any particular product, two fundamental questions must be answered. Will the desired properties of the product remain substantially unaltered, and are significant quantities of harmful radiolytic products formed following irradiation with sterilising doses? The application of radiation chemistry permits these questions to be answered. In general, irradiation in aqueous solution causes more degradation than irradiation in the dry state. Even water of crystallisation increases radiolytic decomposition [44,54,55]. The structure of solids can facilitate radiation induced chain reactions leading to unexpectedly high levels of degradation [54]. Cellulosic materials form an important group of medical products e.g. bandages, swabs, linen sutures, nitrocellulose filters etc., the radiation chemistry of cellulose has been the subject of much research (for a review see [55]. Chain scission of the cellulose occurs and a number of products have been identified following solid state irradiation, amongst which are gluconic acid, glucuronic acid, hydrogen, carbon dioxide and carbon monoxide. Experiments with model compounds have shown that the presence of aromatic molecules can substantially reduce glycosidic chain scission [56,57]. This effect is also evident in plastics where aromatic side groups confer greater resistance to radiation degradation [44].

A number of medical products have been approved suitable for radiation sterilisation in many countries [44] with the prospect of increasing applications of this technique to cosmetics [58] and rising demands for disposable medical products [59]. This area is a fruitful field of study for the radiation chemist.

2.3.3 Tissue banking

Non-viable human and animal tissue grafts are used in treatments to repair damaged body tissue. Hospitals throughout the world routinely carry out cartilage and bone grafting, heart value replacement and middle ear grafting. In addition dura mater is used to treat head injuries and skin is used for dressing burns. Of over-riding importance is the ensured sterility of the transferred tissue and there are a number of methods employed to achieve this end. For successful operation a hospital must have available an immediate source of supply of tissues. Since acquiring and processing tissue is time consuming the only practical solution is to establish a Tissue Bank from which the desired tissues can be supplied on demand. Detailed descriptions of methods of procuring and processing tissue from cadavers are available [60,61]. The thermal lability of tissues rules out heat sterilization and on both scientific and economic grounds irradiation, where applicable, compares most favourably to other sterilizing techniques [62]. A typical protocol for the preparation of bone allografts is shown in Figure 3 [61]. Careful studies on the utilisation of radiation for a number of different tissue preparations have been performed [63]. On irradiation of bone, extremely (lifetime of years) long-lived radicals, detectable by ESR, are formed in the hydroxyapatite regions [64,65]. These radicals can be used to detect irradiated food (see Section 2.4). As grafted bone becomes resorbed, these radicals disappear and ESR measurements have been employed to monitor the healing process [65]. The presence of these radicals and the somewhat reduced mechanical strength of the bone following irradiation do not significantly affect their clinical applications [66].

The various structural components of tissues, viz. proteins, carbohydrates and lipids, have been the subject of intensive investigations by radiation chemists [see 1]. Considerable advances in the understanding of the radiation chemistry of these systems have been achieved. Nevertheless the picture is still not complete although progress continues to be made. The radiation sensitivities of tissues show great diversity, with connective tissue being the most susceptible to radiation induced changes. Connective tissue is the material which fills the space between the cells in skin, tendons, muscles and cartilage. Hyaluronic acid, a polysaccharide consisting of alternating units of N-acetyl glucosamine and glucuronic acid (see Section 2.7.2.) is a major component of the intracellular matrix, and is responsible for many of its vital physical characteristics such as a high visco-elasticity, low permeability etc. [67]. The enormous reduction in the ability of irradiated skin to resist water permeability is shown in Figure 4, where it can be seen that a dose of only a fraction of a Gray causes measurable damage [68].

Similar dramatic radiation induced changes have been observed in lamb vitreous. The vitreous is the clear gel filling the eyeball and is a collagen-hyaluronic acid matrix, and radiation doses of only a fraction of a Gray produce measurable liquifaction i.e. matrix collapse [69]. A prominent feature of the relationship between dose and liquifaction is the clear appearance of a biphasic effect. The intact gel is much more radiosensitive, in terms of liquifaction then the partially degraded gel, resulting in the initial slope of linear liquifaction-dose plots being >10 fold greater than the final slope, the break

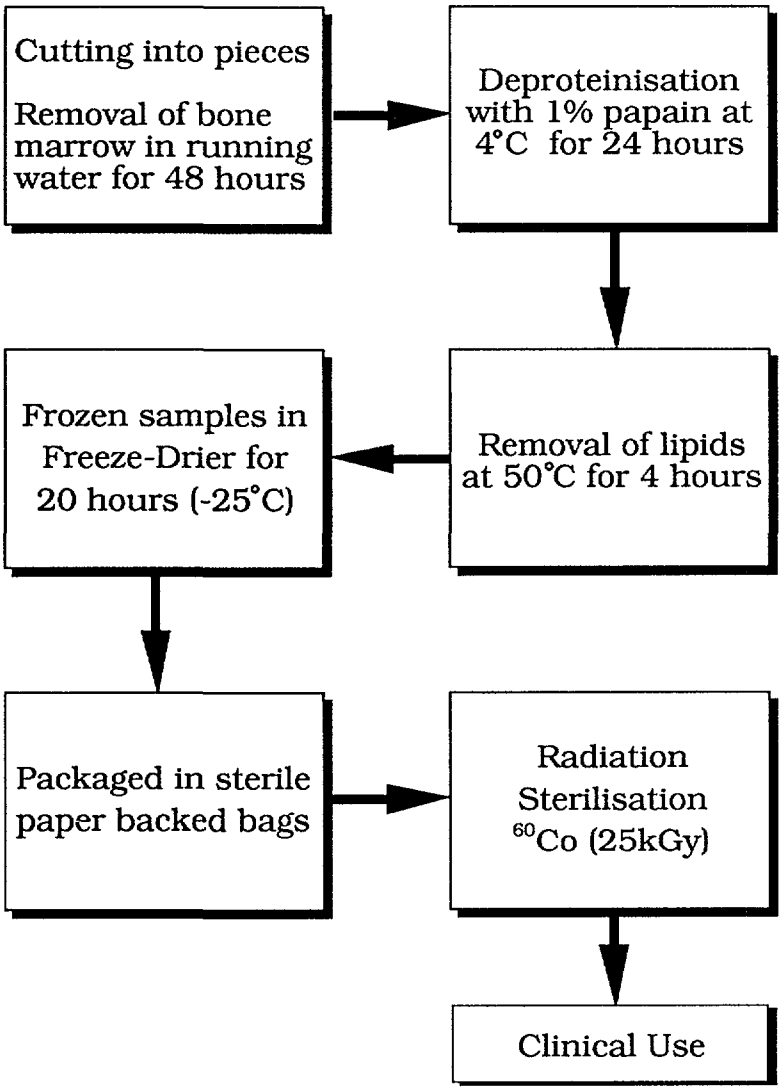

Figure 3. Preparation of bone grafts as described in [61]

point occurring after a dose of ca. 3Gy. A good deal is now known about the radiation chemistry of hyaluronic acid in dilute solution (see Section 2.7.2), in concentrated solutions and in the intracellular matrix, where molecular entanglement occurs thus enhancing the visco-elasticity. One of the main aims of research in this area is to apply the results from aqueous solutions to the biologically important systems and attempts in this direction are already underway [70].

2.4 Development of methods to identify irradiated food

Food irradiation offers the potential of improving food quality by reducing the load of pathogenic and spoilage organisms, by preventing vegetables from sprouting and by delaying the ripening process in fruits. Extensive studies on the preservation of food by ionising radiation have been made over the last 50 years [71]. International and national commissions have examined the safety and wholesomeness of irradiated foods and concluded that within specified

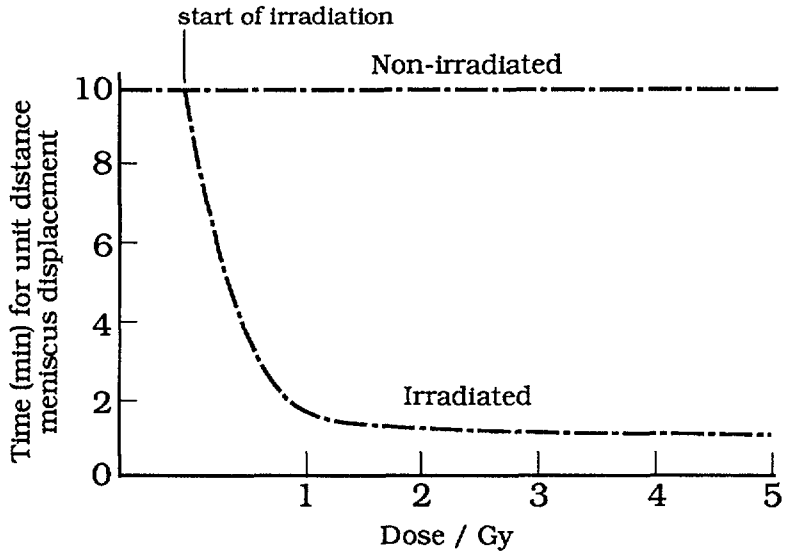

Figure 4. Radiation induced increase in water permeability of connective tissue. The plot shows the change in the rate of water passage, under constant pressure, through rat subepidermal peeled off skin membranes as a function of radiation dose. Data from [68], dose converted to Gy taking 0.97 Gy = 100 Röntgen.

limits of maximum dose and photon/electron energy, irradiated food is fit for public consumption [72-74]. Despite these assurances, objections, many of which are based on misinformation, to the radiation treatment of food continue to be made. As a consequence, the sale of certain irradiated foodstuffs is legal in some countries, whereas in others the sale of any irradiated food is forbidden. The enforcement of such bans requires the availability of a test to distinguish irradiated from unirradiated food. Even where irradiated food can be legally sold, normal trading standards require that the food is labelled in some way to indicate to the consumer that it has been irradiated. Here again enforcement necessitates applying a suitable test. Somewhat surprisingly it is only over the last 5 years or so, that the quest for methods of identifying irradiated food has been undertaken on a wide scale. Radiation chemists (and physicists) in many countries are now involved in developing assays for irradiated food [75,76].

When bone is irradiated long-lived free radicals are formed in the hydroxyapatite region (see Section 2.3.3). These radicals are amenable to detection by ESR. The bones of irradiated chicken and lemon sole and the cuticle of irradiated prawn all gave ESR signals which were not present in unirradiated controls [77]. In the case of chicken bone, the signal even survives cooking. The costs associated with ESR testing are estimated to be in the same range as those for other standard food analyses [78], making it a viable proposition as a routine test.

The practical application of the bone ESR technique has been carefully researched and has been extended to a number of non-meat products (for a review see [77]). In the European Community the BCR (Bureau Communautaire de Reference) has set up an inter-laboratory comparison under the co-ordination of Dr.Raffi, Cadarache, France, to test the practical reliability of these ESR measurements. In the case of chicken bone the trial has been extended to include estimation of the radiation dose. The results of this trial are now being processed. It is, however, clear that for foods

containing bone, the presence of the ESR signal is definitive proof of irradiation although the reliability of dose estimation is not yet clear. Another physical technique, thermoluminescence, which has been used in geological dating for many years, has also proved successful when applied to the detection of irradiated food [80]. Ionising radiation produces separated charge centres and in inorganic solids these become trapped at stable sites. Heating mobilises these centres enabling charge recombination to occur with concomitant fluorescence. By collecting a few milligrams of inorganic debris from a food (e.g. soil or dust) and subjecting it to thermoluminescence measurements, irradiated and unirradiated material can clearly be differentiated [81].

Not all food can be analysed by ESR or thermoluminescence and other possible methods are also being sought. Water is a major component of most foods and water radiolysis leads to the formation of OH radicals, solvated electrons, H atoms, H_2O_2 and H_2 (see Section 2.7). Proteins are present in food and the reaction of OH radicals with the amino acid phenyl alanine produces ortho-tyrosine as one product. It was suggested that the presence of o-tyrosine in food protein could indicate exposure to radiation [82]. Analysis of hydrolysed proteins by HPLC with fluorescence detection has been reported to be successful in identifying irradiated chicken meat from the o-tyrosine content in its protein [83]. DNA is contained in most foods and various avenues of research are being pursued to find a suitable DNA modification as a marker for irradiation [84]. It should be borne in mind that 'OH radicals' can be produced in food by non radiolytic processes (see section 2.7.1) so that the presence of products of ·OH attack on DNA (or any other food constituent) is not uniquely indicative of irradiation. Therefore, it would be better to use products formed either by the reaction of reducing water radicals (H and e^-_{aq}) or by direct ionisation as radiation markers. For DNA, dihydrothymidine is one of a number of possibilities which could serve this function. The irradiation of lipids gives rise to hydrocarbons and cyclobutanones, as the result of direct ionisation or electron capture [85,86]. Techniques have been developed to extract and identify these hydrocarbons in irradiated foods and have been applied to a variety of irradiated samples with considerable success [87]. A method has also been developed to use a cyclic butanone as a radiation marker [88].

2.5 Atmospheric Chemistry

Atmospheric pollution has now become a matter of major public concern. The burning of fossil fuels is responsible for acid rains and smogs. Chlorofluorocarbons, used extensively in the past in commercial aerosol sprays and as a refrigerant, causes stratospheric ozone depletion, thus exposing the earths surface to higher intensities of ultra violet radiation. Finally, there continues to be vigorous debate as to whether increasing atmospheric concentrations of carbon dioxide and other 'greenhouse' gases will result in global warming and catastrophic changes in climate and sea-levels. This latter problem calls for implementing measures for energy conservation, utilising alternative energy sources (including nuclear power) and conserving forests. Radiation chemistry has now an important role in studying these problems.

The major acid constituents of acid rains and smogs are sulphuric and nitric acids [89,90]. Sulphur is released into the atmosphere by combustion of fossil fuels as SO_2 so that its conversion to SO_4^{2-} requires the oxidation of S(IV) to S(VI). Similarly nitrogen undergoes oxidation from NO to NO_3^- [89,90]. SO_2,

NO and NO_2 are not particularly soluble in water which adds to the difficulties of removing them from flue gases. A relatively recent and exciting innovation is employing electron beam irradiation of flue gases to induce the conversion of sulphur and nitrogen oxides to sulphuric and nitric acids which are readily removable. This technology forms the basis of another contribution to this book and will not be dealt with here.

Atmospheric chemistry is extremely complex with gas, liquid and solid phase reactions driven photochemically as well as thermally. The reactive intermediates are often free radicals and radiation chemistry can be utilised to selectively produce and study the properties and reactions of many of these species. The reader is referred to other publications for a full treatment of the subject [89-92]. As an illustration of the type of information that can be derived by careful radiation chemistry studies the aqueous phase oxidation of SO_2 will now be discussed.

$SO_2 + H_2O$	$\rightleftharpoons$	$SO_2 \cdot H_2O$	(24)
$SO_2 \cdot H_2O$	$\rightleftharpoons$	$HSO_3^- + H^+$	(25)
HSO_3^-	$\rightleftharpoons$	$SO_3^{2-} + H^+$	(26)
$HSO_3^- (SO_3^{2-}) + \cdot OH$	--->	$SO_3^{\cdot -} + H_2O\ (OH^-)$	(27)
$SO_3^{\cdot -} + O_2$	--->	$SO_5^{\cdot -}$	(28)
$HSO_3^- + SO_5^{\cdot -}$	--->	$HSO_5^- + SO_3^{\cdot -}$	(29a)
	--->	$SO_4^{\cdot -} + H^+ + SO_4^{2-}$	(29b)
	H_2O --->	$2SO_4^{2-} + \cdot OH + H^+$	(29c)
$HSO_3^- + SO_4^{\cdot -}$	--->	$SO_4^{2-} + SO_3^{\cdot -} + H^+$	(30)

Water droplets in the atmosphere can contain many inorganic and organic compounds, amongst which are iron manganese and copper salts, hydrogen peroxide, and formaldehyde, [89,93,94]. SO_2 hydrates in water before undergoing hydrolysis (reactions 24 - 26). All these equilibria lie to the left so that under natural conditions the sulphur remains gaseous. The oxidation of SO_2 to SO_4^{2-} in solution is thought to proceed by a free-radical mechanism,(reactions 24-30). The initial OH radical could be produced by a Fenton type reaction (metal ion/H_2O_2) or by an OH radical from the gaseous phase of the atmosphere entering the solution. Recently OH radicals have been detected in the Mn(II) catalysed oxidation of S(IV) [95]. Radiolysis experiments have led to the formulation of the scheme shown by reactions 24-30 [96]. Thus S(IV) is converted to S(VI) in a chain reaction. The relative efficiency of this process enables it to compete effectively with the gas phase oxidation of SO_2 despite the low solubility of SO_2. It is clear that for a comprehensive model other reactions must also be considered e.g. $SO_4^{\cdot -}$ + Cl^- radical + metal ion reactions etc. The application of radiation chemistry is the best way of supplying the necessary rate constants and thermodynamic data for many of these reactions.

2.6 Dosimetry

Every application of ionising radiation requires the delivery of a pre-set dose and it is, therefore, of the utmost importance that suitable dosimeters are available. The direct determination of the amount of energy deposited in a given mass of matter requires calorimetric measurements. Calorimetric methods of dosimetry for commercial electron beam irradiators have recently been described [97,98]. Other forms of dosimeter must ultimately be calibrated against calorimeters. Due to their wider applicability in terms of dose range, dose rate and the type of radiation source, chemical dosimeters, where the extent of radiation induced chemical change is used as a measure of the dose, are the most commonly employed. The Fricke dosimeter is the most famous. This relies on the radiation induced conversion of Fe(II) (10^{-3} mol dm^{-3}) to Fe(III) in air-saturated 0.4 mol dm^{-3} H_2SO_4 solutions. [Fe(III)] is readily determined spectrophotometrically. In common with other solution-based dosimeters the presence of small concentrations of organic impurities can cause spuriously high readings and to counter this possibility in Fricke solutions chloride ions (NaCl 10^{-3} mol dm^{-3}) are added to convert OH radicals to $Cl_2^{\cdot -}$ which are less likely to react with the impurity [99,100]. The Fricke dosimeter is well-characterised and is used extensively in basic radiation chemistry research. For high dose rates, often encountered with electron beam sources (i.e. > 10^3 kGy s^{-1}) the so called super Fricke dosimeter (10^{-2} mol dm^{-3} Fe(II), O_2 saturated, 0.4 mol dm^{-3} H_2SO_4) is employed to ensure that reactions with Fe(II) and O_2 compete effectively with radical-radical reactions. In pulse radiolysis experiments dosimetry is routinely performed *in situ* i.e. in the same set-up as that being used for the experiments. When monitoring is optical, the radiolytic yields of transient species such as $(SCN)_2^{\cdot -}$ and $I_2^{\cdot -}$ in KSCN and KI solutions are recorded and used to calculate the dose [101,10]. Dosimetry in pulse-radiolysis with conductometric monitoring is somewhat more complex but can also be achieved *in situ* [102].

In radiation processing it is vital for quality control to record the actual dose received by a particular consignment. The doses administered are generally too large to be determined by the Fricke dosimeter which has an upper dose limit of ca.200 Gy. Other solution dosimeters have been designed to extend the dose range into the commercially useful area. Dilute acidified (0.1 mol dm^{-3} $HClO_4$) solutions of dichromate, in which the radiation induced conversion of Cr(VI) to Cr(III) is monitored spectrophotometrically can be used for dosimetry in the range 2-10 kGy (5×10^{-4} mol dm^{-3} dichromate) and 10-50 kGy (2.5×10^{-3} mol dm^{-3} dichromate) [103]. It was found that the presence of 1×10^{-3} mol dm^{-3} Ag^+ ions prevented side reactions leading to spurious results at higher dose rates [104]. The sensitivity of the dichromate dosimeter can be increased 5 fold, permitting its use for doses as low as 0.2 Gy, by the addition of acetic acid [105]. However, under these conditions measurements must be delayed following irradiation to allow for post-irradiation changes. These may also introduce dose rate effects [106]. Unlike the Fricke dosimeter in which all radiolytically produced water radicals result in Fe(II) oxidation, the dichromate dosimeter measures the difference in yields between oxidising and reducing radicals, the former converting Cr(III) to Cr(VI) and the latter Cr(VI) to Cr(III) [107]. The cerium dosimeter works on a similar principle, with the radiation induced reduction of Ce(IV] being monitored spectrophotometrically, and also is suitable for use in the region 0.5 - 50 kGy [103,106]. Very high doses (> 50 kGy) have been estimated using radiation induced changes in the optical rotation of D-glucose solutions [108].

From a practical standpoint it is often more convenient to use solid dosimeters. Alanine irradiation produces long-lived (almost indefinite lifetime, in the absence of H_2O) radicals detectable by ESR. It is suggested that

alanine could be employed as a dosimeter, the intensity of the ESR signal reflecting the size of the dose given [98,109,110]. A number of polymeric materials on subjection to irradiation yield unsaturated products detectable by spectrophotometry e.g. perspex, cellulose tri-acetate and hence make highly convenient routine dosimeters [103]. Dyed plastics often give rise to radiation induced species absorbing in the visible region and so find great use in routine dosimetry, although great care must be taken in controlling temperature (during and after irradiation) and humidity [103.106]. Radiation induced changes in the electrical properties of silicon diodes has been suggested as being suitable for dosimetric applications in bulk foods [111]. There is a great deal of on-going research activity in the field of dosimetry of which only an indication can be given here. More information can be found in references [103,106,112].

2.7 Free-radical Chemistry

In recent years there has been a growing awareness of the widespread occurrence of free-radicals in many chemical and biological systems. Evidence of the depth of scientific interest in free radicals, particularly their relevance in biology, is reflected in the appearance of a number of periodicals and books dedicated to free-radical research, and the high attendances at meetings of the Society for Free Radical Research which now has over 1200 members world-wide. Radiation chemistry provides the means of generating specific free-radicals and of studying their characteristics. As a consequence radiation chemistry research is of fundamental importance in obtaining basic information for the multitude of free-radical mediated processes now under investigation. Several of these will be considered in more detail.

2.7.1 Peroxidation

Without oxygen most life-forms on earth would not exist. Oxygen can, therefore, rightly be regarded as an elixir of life. Yet, oxygen is, paradoxically, toxic. The toxicity of oxygen arises from its action in inducing and proliferating oxidative damage to vital biological molecules. This process proceeds by free radical reactions, with peroxides being formed as intermediates, hence the term peroxidation. All organic molecules are potentially liable to peroxidative attack, with the extent of damage determined by the chemical structure of the molecule concerned. In order to survive, living organisms have evolved a variety of methods for dealing with oxygen toxicity. These range from the complex systems of enzymes which are capable of repairing damaged DNA, through to the enzymes catalase and superoxide dismutase, which remove prime sources (H_2O_2 and $O_2^{\cdot -}$) of peroxidation, to the synthesis of molecules capable of reacting with intermediate free radicals so preventing them from causing further damage. Compounds falling into the latter category are known collectively as antioxidants. A major constituent of cell membranes is unsaturated lipids and these are highly susceptible to peroxidation. The main function of vitamin E is thought to be as an antioxidant to limit peroxidative damage to the membranes.

Antioxidants act by converting free radicals into stable diamagnetic compounds while themselves being converted into free radicals which are much less reactive than the original and undergo non-damaging reactions. The one-electron oxidation of both vitamin E, its water soluble derivative trolox C [113,114] and the other major natural antioxidant vitamin C (ascorbic acid)

[115,116] can readily be achieved pulse radiolytically. The reactions of the resulting antioxidant radicals can be monitored spectrophotometrically. The antioxidant radicals do not react with oxygen. Ascorbate was shown to reduce vitamin E radicals back to vitamin E with the formation of ascorbate radicals [117]. It has been proposed that in cells, ascorbate radicals, which are relatively mobile, might in turn be reduced by NADH/NAD+, thus ensuring the maintenance of high levels of vitamin E in the membrane with the removal of unwanted oxidising equivalents. The entire process is ultimately under enzymic control.

Since most foodstuffs contain many of the substances found in the organism from which the food originated, it is not surprising that peroxidation also takes place in foods. Those foods with a high unsaturated fat content are especially susceptible to peroxidation, which leads to off-flavours. Oxidative rancidity, as it is known, is of great concern to the food industry and a great deal of research is directed at discovering methods for its inhibition [118].

A general scheme for lipid peroxidation is shown in reactions (31 - 34) where LH is an unsaturated lipid, with H being β to a carbon-carbon double bond.

$$LH + \cdot OH \text{ -------> } L\cdot + H_2O \quad (31)$$

$$L\cdot + O_2 \text{ -------> } LO_2\cdot \quad (32)$$

$$LO_2\cdot + LH \text{ -------> } LO_2H + L\cdot \quad (33)$$

$$LO_2\cdot(L\cdot) + LO_2\cdot(L\cdot) \text{ ------> products} \quad (34)$$

$$LO_2\cdot + AH \text{ -------> } LO_2H + A\cdot \quad (35)$$

Peroxidation proceeds via a chain reaction in which reaction (31) is the initiating step, reactions (32) and (33) are chain propagators and reaction (34) is chain terminating, and represents all three possible radical-radical reactions. Although an OH radical is shown in reaction (31) other radicals could also perform this role. It has been well-established that Fenton type reactions (reduced transition metal ions plus H_2O_2) produce OH radicals or pseudo OH radicals. $O_2\cdot^-$ is a source of both reduced metal ions and H_2O_2. In biological systems $O_2\cdot^-$ is formed by enzymic reactions and the direct reaction of reductants with oxygen. Organic peroxyl radical reactions provide an additional supply of $O_2\cdot^-$ [119], so that in oxygenated biological systems $O_2\cdot^-$ is in fact ubiquitous. The hydroperoxide formed in reaction (33) is unstable and its decay products are responsible for off-flavours [118]. Ferric ions appear to induce the conversion of lipid peroxides to aldehydic products and simultaneously, in the presence of unsaturated lipids and oxygen, promote further peroxidation [120].

Antioxidants perform their function by reacting with $LO_2\cdot$ radicals (reaction 35), where AH is the antioxidant), thus preventing the chain reaction (reactions 32 and 33). Many foods contain the natural antioxidants vitamins E and C. Supplements of these vitamins are also frequently added to foods during processing [118]. A number of synthetic antioxidants have also been approved by many countries as food additives. The most commonly used are butyl hydroxy anisole, butyl hydroxy toluene, butyl hydroquinone and n-propyl gallate.

Radiation chemical investigations have contributed to an understanding of the chemistry of n-propyl gallate. Superoxide radical anions ($O_2\cdot^-$) produced pulse

radiolytically react with n-propyl gallate (3,4,5 trihydroxy n-propyl benzoate) or the structurally related compound, pyrogallol (1,2,3 trihydroxy benzene) [121]. At relatively high concentrations of n-propyl gallate and low $O_2^{\cdot -}$ concentrations (i.e. low dose), the initial transient species has an absorbance maximum at 420 nm, whereas at longer times, lower n-propyl gallate concentrations and higher $O_2^{\cdot -}$ concentration (high doses) a transient with an absorbance maximum at 550 nm is observed (see Figure 5). By comparison with the absorption spectrum of the n-propyl gallate phenoxyl radical (formed by reacting 1 electron oxidants with n-propyl gallate) the initial transient (λ_{max} = 420 nm) was identified as being this phenoxyl radical. Reaction of the phenoxyl radical with $O_2^{\cdot -}$ resulted in the appearance of the transient with λ_{max} 550 nm. The complete reaction scheme is shown in Figure 6. Computer modelling was used to obtain the rate constants of the reactions. The rates of absorbance changes at 420 nm and 550 nm were measured for three different n-propyl gallate concentrations each containing three different $O_2^{\cdot -}$ concentrations and the values of the rate constants giving the best fit were determined [121]. A typical correlation between simulated and experimental data is shown in Figure 7. As noted $O_2^{\cdot -}$ participates in peroxidation, so the ability of n-propyl gallate to remove $O_2^{\cdot -}$ would augment its antioxidant capacity. In this respect, it is interesting to note that vitamin C appears to behave similarly [122].

Antioxidants by definition are relatively easily oxidised and on heating in air undergo decomposition. Food processing often necessitates heating, resulting in loss of antioxidant activity. By encapsulation in cyclodextrins (six to eleven member cyclised 1-4 glucose oligosaccharides) the stabilities to

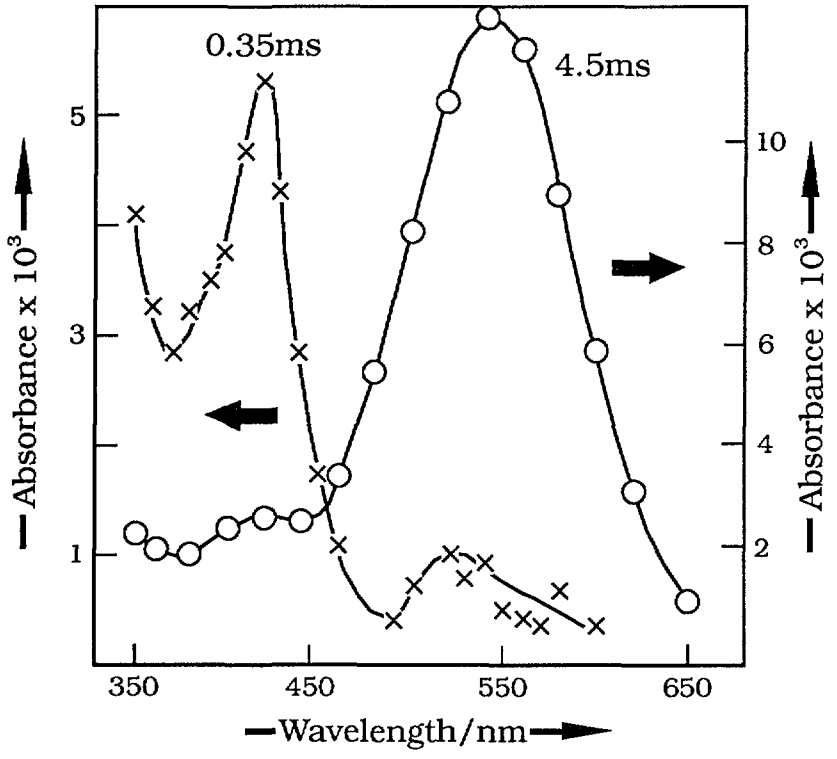

Figure 5. Transient spectra on reaction of $O_2^{\cdot -}$ with n-propyl gallate at pH 6.8. (0.7 mol dm^{-3} formate, N_2O/O_2 (4:1), 2 x 10^{-3} mol dm^{-3} phosphate: x, 5 x 10^{-3} mol dm^{-3} n-propyl gallate, 0.35 ms after 1.9 Gy pulse; O , 2 x 10^{-3} mol dm^{-3} n-propyl gallate, 4.5 ms after 17.8 Gy pulse. All absorbances normalised to a pulse of 10 Gy. Taken with permission from [121]

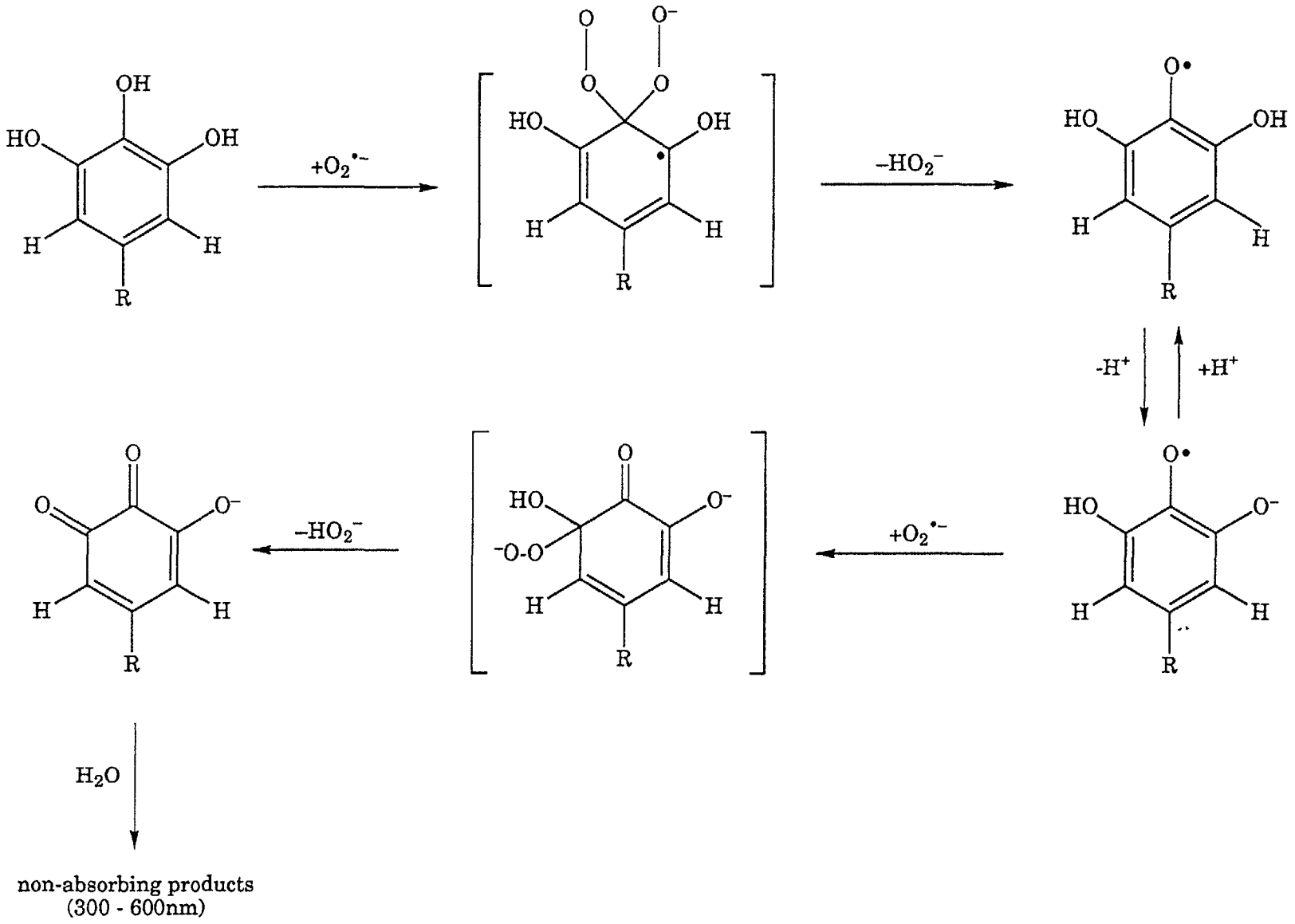

Figure 6. The reaction of $O_2^{\bullet -}$ with n-propyl gallate (R = –CO –n propyl)

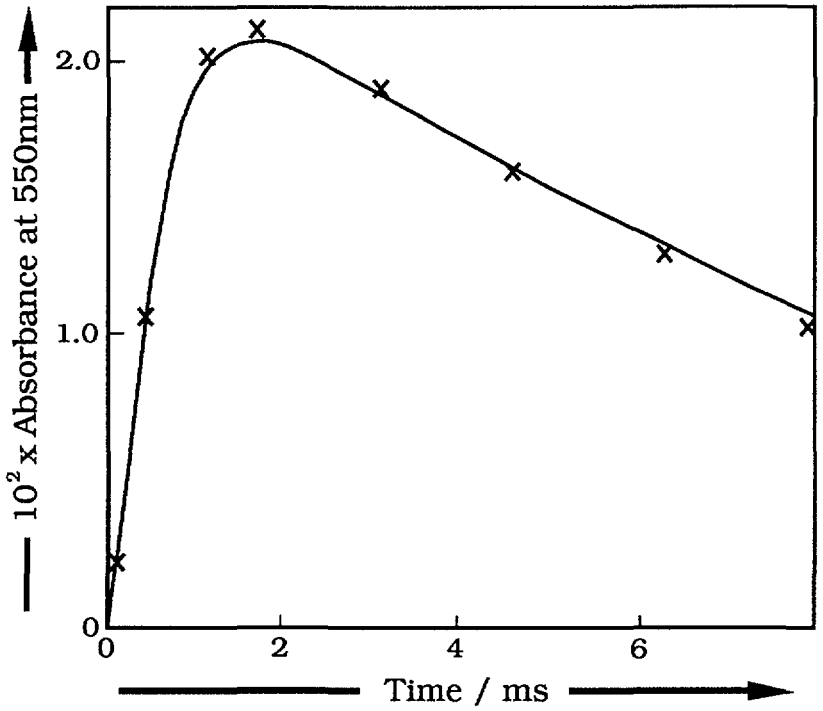

Figure 7. Comparison of measured (x) and calculated (solid line) absorbance change at 550 nm for n-propyl gallate reacting with $O_2^{\cdot-}$ according to the proposed mechanism. (5×10^{-3} mol dm^{-3} n-propyl gallate, 0.7 mol dm^{-3} formate, 2×10^{-3} mol dm^{-3} phosphate, pH 6.8, N_2O/O_2 (4:1), dose 19 Gy)

oxidation, volatilisation etc, of a number of useful aromatic compounds have been improved. It was possible to encapsulate n-propyl gallate, butyl hydroxy anisole, and butyl hydroquinone in β-cyclodextrin [123]. Pulse radiolysis was employed to generate the corresponding encapsulated phenoxyl radicals. The rate constants for self-termination reactions were substantially reduced in comparison to the free phenoxyl radicals. For n-propyl gallate the reduction is more than 1000 fold. Based on the ability of the antioxidants to repair the tryptophan radical, it was shown that the encapsulated antioxidants continue to function as efficient reductants. Encapsulated n-propyl gallate reacts with $O_2^{\cdot-}$ but no subsequent reaction of the resulting phenoxyl radical with a further $O_2^{\cdot-}$ occurs. Thus the free radical chemistry indicates that encapsulated antioxidants retain their functionality. Whether encapsulation reduces oxidative degradation of the antioxidant remains to be answered.

2.7.2 Hyaluronic Acid Degradation

Hyaluronic acid is a major constituent of connective tissue. It is a high molecular weight polysaccharide consisting of alternating subunits of 2-acetamido-2-D-deoxyglucose (β-1--->4 linked) and D-glucuronic acid (β-1--->3 linked) as shown in Figure 8. Many of the biological functions of hyaluronic acid e.g. lubrication and molecular exclusion, stem from its ability to retain water and form viscous solutions, a characteristic which is strongly dependent on the hyaluronic acid chain length. In certain diseases of the joint such as rheumatoid arthritis, synovial hyaluronic acid is degraded. The numbers of polymorphonuclear leukocytes in synovial fluid increases during the course of

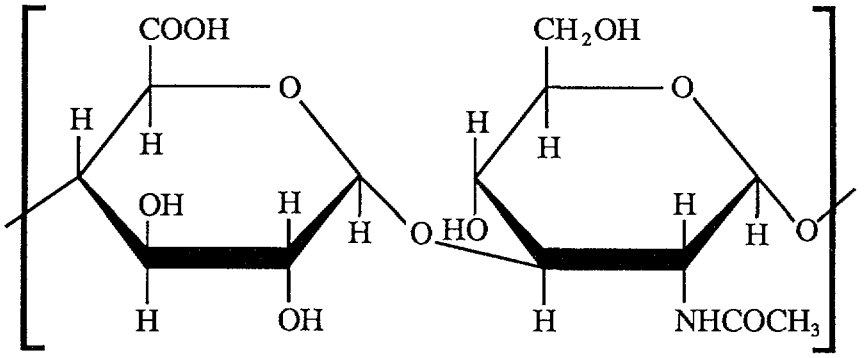

Figure 8. Hyaluronic Acid Dimeric Repeating Unit

these diseases and their release of superoxide radicals in phagocytosis is believed to be associated with hyaluronic acid degradation [124]. Indeed synovial fluid has been shown to be degraded by enzymically produced $O_2^{\cdot -}$ with protection afforded by the enzymes catalase and superoxide dismutase [124].

As noted in Section 2.7.1 transition metal ions in biological systems are thought to interact with $O_2^{\cdot -}$, and its dismutation product H_2O_2, to yield OH or OH-like radicals which initiate further reactions. The levels of iron and copper ions in the synovial fluid of rheumatoid arthritis sufferers are higher than those in healthy people [125-127]. Elevated concentrations of both $O_2^{\cdot -}$ and transition metal ions in the synovial fluid increases OH (OH-like) radical formation. Reactions of these radicals with hyaluronic acid ($k(\cdot OH$ + hyaluronic acid) = 8.8 x $10^8 dm^3\ mol^{-1}s^{-1}$) results in the formation of hyaluronic acid radicals [129]. Subsequent reactions of these radicals lead to chain scission. Radiation chemistry techniques have been employed to investigate these processes [129-133].

The fraction of hyaluronic acid radicals in aqueous solution at pH ca. 7 leading to chain scission is reduced by the presence of oxygen (see Figure 9). A protective effect of similar magnitude is conferred by substituting the oxidant, tetranitromethane, for oxygen [131]. The radicals produced in hyaluronic acid by OH radical attack are α-hydroxy (or α-alkoxy) carbon-centred radicals which react rapidly ($k \sim 10^9 dm^3 mol^{-1}s^{-1}$) with oxygen and tetranitromethane. It would seem, therefore, that one or more hyaluronic acid radicals are prevented from conversion to a chain break by these reactions. A possible candidate is the radical at C-6 of the glucose subunit. In the absence of oxygen (or tetranitromethane) β-scission and subsequent hydrolysis of the resulting C-3 radical would lead to a chain break. The C-6 peroxyl radical formed by O_2 addition would result in the formation of the C-6 aldehyde and no chain scission. Tetranitromethane would have the same effect.

By applying pulse radiolysis techniques, the process of strand cleavage can be followed directly. At pH > 5 hyaluronic acid exists in solution as a polyanion due to the negatively charged carboxyl groups. It had been shown previously for nucleic acids which are also polyanions, that chain scission resulted in an increase in conductivity as condensed counter-ions are released from the broken ends [134]. This effect also occurs with hyaluronic acid, enabling the kinetics of chain breakage to be determined using pulse radiolysis with conductometry [132,133]. In the absence of oxygen, the overall rate constants for strand breakage vary considerably with pH (Figure 10). The reaction seems to be acid/base catalysed, suggesting it might be of a hydrolytic nature e.g. the hydrolysis of radicals sited at the carbon atoms

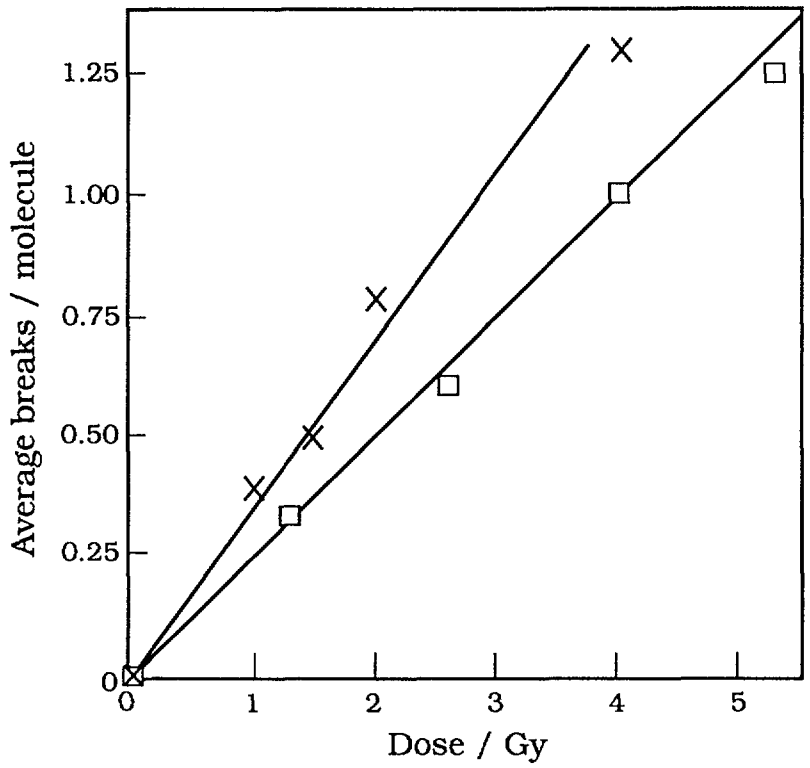

Figure 9. Radiation induced strand breakage in hyaluronic acid (2×10^{-3} mol dm^{-3} in disaccharide units, $\bar{M}n$ before irradiation = 1×10^{6} Da, pH 7, 2×10^{-3} mol dm^{-3} phosphate, 0.011 Gy s^{-1}): x, N_2O; □, N_2O/O_2

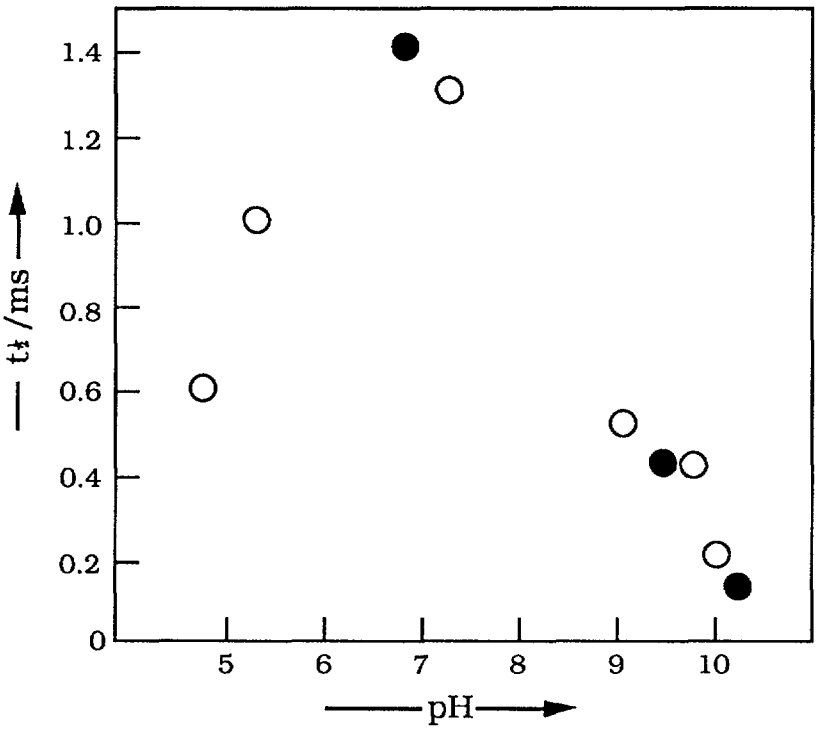

Figure 10. pH dependence of the rate of chain scission (expressed as overall half-time for the reaction) in hyaluronic acid radicals in the absence of oxygen: ○, no buffer; ●, 2×10^{-3} mol dm^{-3} phosphate Taken with permission from [133]

involved in the glycosidic linkages. In the presence of oxygen strand scission is base catalysed, but the process is complicated by the apparent involvement of both kinetically first and second order reactions in rate determining steps [133].

Measurements made using pulse radiolysis in conjucntion with low angle laser light scattering permit fragmentation to be observed directly [133]. As shown in Figure 11 the yield of chain breaks, in the presence of O_2, increases with increasing pH. The reason for this is not yet known. Of some importance is the fact that in the presence of oxygen over half of the hyaluronic acid radicals are converted to $O_2^{\cdot -}$, thus replenishing the $O_2^{\cdot -}$ concentration and *in vivo* increasing the likelihood of further hyaluronic acid radical formation (via 'OH' radical attack) [133].

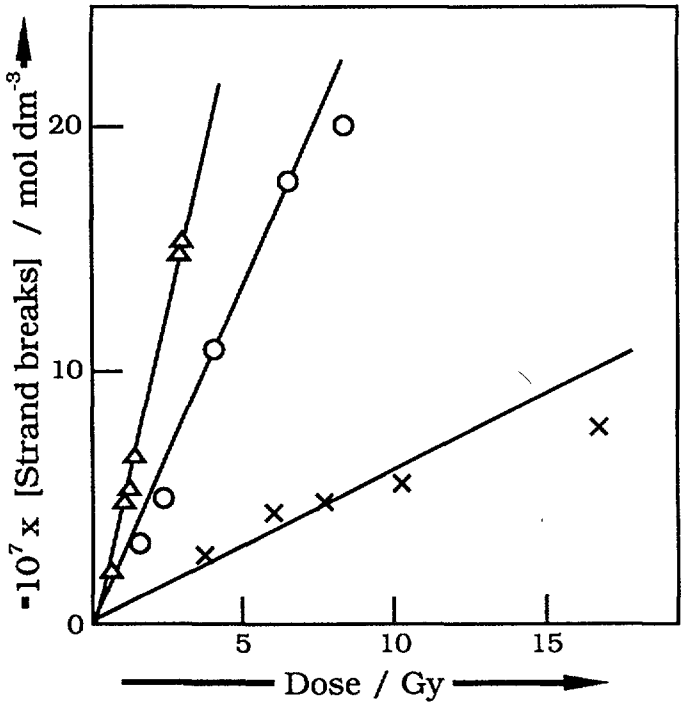

Figure 11. Yield of chain breaks as a function of dose per pulse, for pulse irradiated N_2O/O_2(4:1) saturated hyaluronic acid solutions: x pH 7,;o pH 9.7,;△ pH 10.4,taken with permission from [133]

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PRESENT AND FUTURE PROSPECTS FOR RADIATION

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Abstract

The future trends of research in radiation chemistry are analyzed on basis of past and recent advances in this discipline. After consideration of available radiation sources and their capabilities, special attention is afforded to the effects of ionizing radiation on polymers. Topics of interest for consideration were advances in: radiation-induced main chain scission, crosslinking and network formation, polymerization, graft polymers, irradiation in solutions, and radiation curing of polyesters. The potential of new practical applications resulting of suggested research activities are indicated. Some attention is afforded to the potential of food irradiation. It is concluded that continued research in selected areas will result in the development of higher radiation resistant and fire-retardant cable insulations, new composite materials, polymers of higher strength, the formation of complex three-dimensional structures in certain polymeric materials, foamed materials with controlled pore size, and grafted films for chemical control, such as catalysts.

INTRODUCTION

Exposure to an intense beam of high energy radiation can promote three major types of change in materials; a change in nuclear structure, a change in the arrangement of such nuclei as in the modification of crystalline structure, and finally changes in electronic arrangement. These can lead to the production of ionised species, with free or trapped electrons and subsequent luminescence, electrical discharge phenomena and conductivity, as well as reactive chemical species such as radicals and ionised species with consequent chemical reactions leading to further physical, chemical and biological change.

For the present purposes we are primarily concerned with this third group and not at all with any nuclear changes; indeed we seek to avoid long-term radioactivity wherever possible. In the present context we are attempting to produce sufficiently large quantities of the purely chemical reactive species to result in substantially modified or novel chemical, physical or biological properties in the irradiated material. In the present context one would therefore exclude trace radioisotopes which, despite their considerable value, are to be considered as advanced tools of analysis for use with very sensitive radiation detectors, rather than as new or modified products in their own right.

The study of such irradiated products forms a major part of what is now considered as the subject of radiation chemistry, although the largest scale applications so far have fallen in two related sciences; mechanical and electrical properties of polymeric materials and certain biomedical applications as in sterilisation. Indeed one might claim to see two divergent directions of future progress; basic radiation chemistry which is primarily of fundamental and academic interest and forms a most interesting new branch of pure chemistry, and especially of chemical kinetics and reaction mechanisms; and more directed or

applied work where one can take advantage so some of the unique advantages of high energy radiation to produce new materials, or improved methods of providing well-established older products. Here one can also include the use of such irradiated materials to relate known resultant structural changes caused by radiation to any resultant modification in physical, chemical or biological properties being investigated. These can then be better understood from their chemical causes. Examples are the changes in mechanical behaviour with degrees of crosslinking or molecular weight, from highly elastic to glassy; the degrees of protection or enhancement in biological systems resulting from selected additives; and polymerisation or oxidation rates in the presence of additives.

In some instances the causes of certain important radiation-induced processes are still not fully understood at the purely scientific level. For example, the crosslinking of polymers, possibly the most rewarding application of radiation, although an apparently simple reaction, is still not properly intepreted in terms of a sequence of chemical reactions, even after more than four decades. On the other hand one sees published other radiation chemical processes studied in the greatest detail by such fine techniques as very fast pulse radiolysis, although the purpose of studying a specific reaction with certain components is not always made very clear in the accompanying published text. Indeed one feels that these two approaches, the more academic and the more practical are gradually drawing apart, a most unwelcome situation. From the present point of view this implies that we shall be more concerned with the second outlook. As editor-in-chief of the leading scientific journal in the field of Radiation Physics and Chemistry, I find myself increasingly having to suggest that potential authors should try and make clear to a potential reader why he should be interested in the reaction they are investigating and the solution they are attempting to provide. I hope that this comment will not be directed at me!

In trying to forecast future trends in the development of Radiation Chemistry processes we must look back and see which applications have been most successful and which have been disappointing and why. Certainly the most effective have been the crosslinking of polymers and the sterilisation of medical disposables. Both involve minute chemical changes but which result in great physical (mechanical) and biological improvements (at least from the human point of view!). So one most important common feature is an enhancement in effect when dealing with systems with high molecular weigth molecules; the chemical change may be very small but the change in morphology can be immense, as in the survival of a bacterium or the transformation from a soluble to a non-soluble system, and from a flowing to an elastic polymeric composite. This permits an additional and very flexible method of quantitative control of a reaction at any stage of the complete process. Biologically imposed crosslinking and network formation of rubber molecules within the tree itself would not present great practical value, except possibly to those who like to lean on them!

The second field of interest has been where radiation has been used to provide chemical initiating species from which a chain reaction ensues. This special advantages of radiation as

initiator must then be carefully assessed in comparison with competing processes such as photochemical initiation. With radiation one has far fuller control on such factors as temperature allowing reactions to be initiated in the solid or glassy state, over an immense range of dose rates and for materials of any desired thickness and without special absorbing species, and then following the ensuing reactions at various temperatures. However, the high initial cost of the installation represents a serious disadvantage in entering this field.

Here we see the two distinct streams emerging. Both require relatively small inputs of radiation energy, tens of kGy or some Mrads or less. In one the correspondingly low number of chemical changes is quite adequate to produce the desired change, usually physical or biological in nature; the other stream allows for small radiation-induced changes to initiate large scale chemical reactions as in polymerisation, or in the curing of unsaturated polyester systems; here the chemical formulation is far more critical and can be intrinsically much more expensive. These two streams must be discussed separately; the problems involved are quite distinct.

On exposure to high energy radiation, in particular to high energy electrons or gammas of the order of one MeV, it is generally assumed that energy is absorbed almost at random within irradiated organic structures yet that it is then channelled according to some physical programme as yet incompletely understood, into specific chemical bonds so that very different chemical changes ultimately result. In the case of polymers, as indeed in lower molecular weight compounds, there are several routes that this energy can follow, and the routes chosen are not necessarily those based on the strength of the chemical bonds which are eventually ruptured. In addition the electron ejected during ionisation may be trapped and eventually result in such phenomena as thermoluminescence or electrical discharge or other electrical or optical effects. Here we are more concerned with long-term changes resulting from these chemical modifications, even when these cause mechanical modifications (elasticity and creep) or biological improvements as in sterilisation.

Of many possible radiation-induced modifications in chemical structure the apparently simplest and most valuable to date have been those occuring in flexible linear polymers and they can be ascribed either to scission of the main chain with a progressive reduction in average molecular weight (degradation) with corresponding change in physical properties; and alternatively to an increase as chains become linked together by rupture of side chains (crosslinking) leading eventually to the formation of a network. The transition can be followed step by step using increasing doses. In most polymers one or another of these reactions dominates to a large extent and only in such an instance as polypropylene is a polymer half-way between these extremes; as might indeed be expected from its chemical structure between the crosslinking polyethylene and the degrading polyisobutylene.

Other reactions may also be envisaged such as changes in main chain unsaturation or possibly with very low doses, a rapid decrease in initial unsaturation as in polyethylene. This is not

necessarily a radiation-induced reaction, but may be due to the gaseous product, H or H_2O engendered by the chemical reaction of the polymer, leaving this product present to continue its reactions elsewhere in the system.

A further advantage of such investigations is that, once the basic reactions have been analysed and understood, the effect of parameters can be investigated, including such factors as dose and dose rate, irradiation in the presence of oxygen, the effectiveness of additives in reducing the oxidation reaction or directing it in different directions. Alternatively one can envisage a situation where the additive greatly enhances the effect of radiation or its sequel, leading to other reactions in which radiation is only the initiating step, but one which is under full control.

Another view of radiation effects which parallels some aspects of Radiation Chemistry may be termed Radiation Physics. This has not reached the industrial stage of development of radiation chemistry with its associated physical and biological applications. Radiation Physics is more concerned with the displacement of nuclei and of electrons and their trapping on a more permanent basis. This aspect has been developed in several directions. Irradiation of semi-conductors already shows considerable promise. It results in an improvement of short-term switching and of the lifetime of carriers in power semiconductors, and even in an adjustment of properties of such devices manufactured by other means.

The coloration of diamonds and other precious stones has long been known and glass tiles, coloured by exposure to radiation have been installed in public buildings in cases where coloration by conventional chemical methods would not be possible. The material used and its long-life behaviour when exposed to intense u.v. light must be examined. One may envisage an extension of this use with a variable electron beam scanning across the tile to inscribe permanently a pattern within it.

Efforts are now being devoted to the irradiation of metallic oxides for use in catalytic processes as well as irradiation of their carriers. One may envisage an improvement of catalytic behaviour but this has not yet reached an industrial level.

Claims have also been made for extremely fast and local heating with a powerful electron beam; heating to the melting point in 1 ms, far faster than heat can leak away, followed by very rapid cooling at 50000C/sec. Exposure of metals and their alloys may give an unusual form of surface treatment, with claims of improved surface properties for mechanical use, or for very high purity treatment. One may also envisage surface treatment of reinforcing fillers such as silica.

POTENTIAL FOR RADIATION INVESTIGATIONS

For a majority of applications, high energy radiation can be considered as a method of initiating chemical reactions via radical or ionic initiators under very favourable conditions. Among the advantages one may note the following:

1) No chemical additives are needed to initiate the reaction.
2) No residues from chemical reagents need be left; where new byproducts such as H_2O result from a radiation-induced reaction, they only occur in very small amounts and are usually innocuous.
3) An enormous range of intensities is available, from 2μsec to days, far greater than can be obtained in chemically initiated reactions;
4) In most cases the reactions show little dependence on temperature. This provides an extra degree of freedom so that for example it is possible to have two reactions, one radiation initiated, the other chemically, and use the first radiation step to formulate the conditions under which the second chemically initiated reaction can proceed. Conversely a chemical process resulting from radiation can follow the engineering stage.
5) Reactions can take place in the solid, liquid or gaseous state or in solution, and secondary reactions can be produced from reactions in the solvent.
6) Differential effects can be organised to occur within the same specimen. For example one may treat a certain thickness from the surface by choosing the appropriate voltage of an electron beam, and modify the underlying body to a different extent with electrons of a different voltage and penetration. There is also the possibility of sweeping the electron beam across the specimen while modifying its intensity, thereby constituting a form of volume painting.

Many of these and additional potentialities have still not been adequately studied for new applications or even been explored but should provide a very wide new scope for investigating possible modification of materials.

We see several widespread applications widely used over many years; crosslinking of polymers such as polyethylene and partial vulcanisation of rubber; foamed polyethylene; sterilisation of medical devices such as disposable syringes where radiation treatment offers marked advantages over chemical sterilisation. Other major applications being introduced gradually in different countries include food sterilisation and disinfestation, sterilisation of medical devices such as bandages, production of membranes for chemical processes, surface curing of paints or other surface reactions without a heating stage or even a solvent to evaporate. Numerous research programmes envisage the use of radiation in processes such as sewage disposal and treatment of harmful gases, the surface modification of textiles by grafting of the fabric, an improved wood product by the incorporation of suitable monomers, which are then polymerised and grafted into the wood by radiation. Likewise there is growing interest in the crosslinking of polymers otherwise difficult to form into a network by the introduction of polyfunctional monomers which react by a chain reaction so that a very dense network results from a small dose and without heating.

In addition we can envisage new lines of research in which these advantages can be used to improve our understanding of the properties of materials. For example we now have a means of controlling quantitatively the formation and characteristics of a range of glasslike systems and studying how far these can be

linked up with the ensuing properties such as the diffusion of gases.

Here we can only discuss a few of these projects. The most up-to-date and widest survey can be obtained from the periodic conferences and especially from the periodic International Meetings on Radiation Processing attended by both academic and industrial experts, and also from more specialist conferences which are often published in the scientific press as a permanent and widespread record of the present situation. Selected books are usually of a more academic nature and deal with the reactions involved. Special issues of scientific journals, each dealing with only one topic and intended to present the present outlook of a number of worldwide experts on that topic, probably provide the best source of up-to-date information not only on matters already settled but equally important those on which even these specialists have not yet agreed.

Only a few of these topics can be dealt with more fully here.

RADIATION SOURCES

To date we have to deal primarily with only two types of large-scale sources; 1) those based on the radioactive decay of radioactive Cobalt 60 with a half-life of 5.3 years and emitting penetrating gamma radiation of 1.3 MeV and 2) electron accelerators which fall primarily into (a) lower voltage machines typically between 150 and 400 keV and (b) those producing higher voltages of between 1.5 or 2 and about 10-14 MeV.

The radioactivity of a typical Cobalt 60 research installation would lie between 1 and 50 kcurie, corresponding to a gamma power output of 1.48 and 74 watts. These gamma sources often consist of a series of cobalt rods which can move together from a safe position into the chamber in which specimens are to be irradiated. Both sources and specimens to be irradiated are housed within a chamber or room provided with heavy concrete walls and ceiling to protect operators outside. Access is gained via a passage through a series of bends, with a gate which can only be opened when the sources are all in a safe position. Other equivalent arrangements are possible, a most useful feature being that a range of dose rates is available, from several Mrads (tens of kGy) per hour downwards.

In another type of construction a heavy shielded metal container is provided into which the sample to be irradiated can be inserted; the source is also located within this container. This construction has certain disadvantages such as small specimen size and poor accessability with restricted space for auxiliary equipment, but it does permit installation in a conventional laboratory without extra shielding.

An industrial radioactive cobalt equipment would comprise several megacuries with a power output of kilowatts. The whole installation comprises a large number of radioactive sources installed along a series of rows within a large shielded chamber through which the samples for irradiation are moved on a conveyor

system or by containers hanging from an overhead track. In most cases the radiation level is relatively low, of the order of tens of kGy (Mrads) per hour and the high output needed in an industrial installation is achieved by the large amount of material being processed simultaneously.

Several types of electron accelerators are available with very different characteristics but they may be considered to fall into the following main groups:

a) The lower voltage machines with corresponding low penetration, of a fraction of a mm in material of unit density. Such electron equipment would serve primarily for the study or treatment of thin sheets and films or surface reactions. The shielding needed for the protection of personnel is correspondingly reduced and the entire equipment can often be installed in a production working line. However, the low penetration imposes a serious limit on the type of process for which it is appropriate.

b) Accelerators of various types but usually producing about 2-4 MeV were largely used in the earlier researches and in production. At present higher voltages are used for such investigations as pulse radiolysis with powers of the order of a kw and with penetrations of about 1 cm in matter of unit density. For industrial use the pressure has been on increasing power, at present often amounting to several hundreds of kw, since the cost of the installation including shielding does not increase in proportion to power output.

c) A third group of accelerators comprises higher voltage equipment with higher penetration but usually lower power. They would be used when their higher penetration is essential but also when nuclear reactions may be involved. Other special qualities may also be desired.

d) A fourth group is in the intermediate region in the neighbourhood of 0,6 to 1 MeV. There is strong need for a powerful source with this type of penetration, but it seems to be lacking. One hopes it could be manufactured with high power and at lower cost than the 2 MeV group, but for applications where the first group up to 400 KeV lacks penetration.

For certain purposes, as for example in polymerisation, where the net chemical effect can be strongly dependent on dose rate, a low dose rate, allied to a long exposure time and a large amount of material being treated simultaneously appears as most suitable. For such applications gamma radiation is most appropriate. In other applications a very rapid, high intensity electron beam is preferred since the radiation chamber may be smaller and shielding easier. Such conditions may also appear more suitable when long exposures could increase undesirable side-reactions such as oxidation.

Where output is determined primarily by total dose absorbed and far less by other factors, the possible cost of a potential industrial treatment can often be assessed at least approximately from the cost of radiation per kwh. The capital write-off may constitute a major part of the total installation cost and an over-simplified calculation can be made. For an installation costing say D million dollars (equipment) and I million dollars (installation), written off over 10 years, an output of 100 kw at 20 hours per day and 250 days in each of ten years, the

capital repayment cost per kwh might be $(D+I).10^6/50\ 000$ x 100 = $(D+I)/5$ dollars per kwh, ie of the order of a dollar/kwh. After allowing for overheads, repairs and staff a higher figure is reached but a very rough estimate of several dollars per kwh is often approached, dependent on utilisation and efficiency of energy absorption, as well as other charges, very dependent on application.

A kwh of absorbed energy equals an average of 360 Mrad.kg or 3600 kGy.kg but not all of this will be absorbed in the specimen. Assume that the dose requirement averages r Mrads or 10r kGy, the efficiency of utilisation is e and the cost of high energy radiation amounts to d dollars per Kwh. The cost of radiation treatment then amounts to 100dr/360e cents per Kg. Thus in radiation sterilisation, where r=2.5, e=0.5 and d=2 about, the cost per kg would be about 3 cents. In radiation crosslinking, with r about five times higher, the cost might be 15 cents. Obviously these can only be very approximate figures but they emphasise the advantages of using low cost accelerators and maximum utilisation of large irradiation sources. It does appear that capital repayment on equipment is the major cost rather than running expenses. Another major cost may be the transport cost to and from the large radiation centre for radiation treatment of foodstuffs collected from a large area, though they could be distributed directly from the radiation centre. Surface treatment requiring electron beams of lower voltage and lower installation cost might appear most profitable, but the crosslinking of film or cable at large centres has to date proved the major money-spinner.

One of the great advantages of radiation is its ability to penetrate and carry out reactions inside the solid or more rigid state. The lesser dependence on temperature and the lack of any initiators or other additives can be of considerable advantage in competition with possibly competing processes such as photochemistry with ultra violet light or plasma discharge reactions which might have the advantage of considerably lower capital and installation costs.

Electron accelerators with a swept electron beam have been the major source of electrical radiation and one wonders whether a less technically advanced equipment might provide an additional and less costly alternative for certain applications such as the treatment of liquid residues, where uniformity of dose is not absolutely essential.

For certain purposes irradiation with heavier particles, or with far higher energies to promote nuclear displacement, modification of electron trap depth (for semiconductor or other electrical modifications), changes in crystal structure or even the production of radioactive nuclei etc may also be envisaged, but at present the above appear by far the most rewarding of large-scale industrial applications.

RADIATION-INDUCED MAIN CHAIN SCISSION

A number of polymers show main chain scission (degradation) as a permanent effect of exposure to high energy radiation. This

reaction is relatively simple to follow in linear polymers since excellent methods are available to determine the molecular weight (number average) of initial and irradiated polymer and its reciprocal should show a linear rise with dose, as is indeed found over a very wide range;

$$1/M_o = 1/M_{no} + 1.04.10^{-7}.G\ r.$$

Here r is the dose in kGy (0.1Mrad) and G the number of scissions per 100 eV absorbed energy. G values in the neighbourhood 1.5 to 3 are common and are to be compared to the number of ions G(ion) formed in irradiated gases. In solids or liquids G(ion) is usually far lower; the ejected electron loses energy rapidly by collision with neighbouring atoms and only rarely is it able to escape the field of its parents; instead it returns to form an excited unstable entity or less frequently it is trapped. This may serve to explain the approximate similarity of G(ion) in irradiated gases and G(radical) in irradiated solids or liquids, even for molecules of similar structure. It is still somewhat significant that such a high proportion of the initial ionisations should appear to end up as excited systems following recapture.

The very extensive range over which this linearity is observed, possibly as far down as molecules of only a few monomer units, is highly significant. Each scission is independent of the others, and no cooperative reaction is involved as in depolymerisation. There remain a number of important questions to be settled:

1) Does main chain scission occur equally readily in chains lying in the more rigid crystalline regions as in the more flexible amorphous regions? Experiments with PTFE (see below) appear to answer this question.

2) There is a small but significant temperature dependance of G(scission). To which physical process in the polymer is this to be ascribed? Is it due to lower energy requirement or to more free volume allowing broken chain-ends to separate?

3) In glassy polymers which scission, the reduction in molecular weight is only measured when the temperature is subsequently raised. Does this mean that the scission does in fact occur during irradiation, or are reactive species trapped in the glass, only able to produce the final main chain break and separation of ends when higher chain mobility becomes possible? And if so, what is the nature of this potentially reactive species?

4) Assuming that scission does in fact occur during radiation, what keeps apart the broken and highly reactive chain ends at the point of scission? Two different explanations may in fact be involved; in glassy or crystalline polymer and in flexible polymer.

5) This raises the further question of energy or reactivity transfer in such systems but this may be a more general topic, not confined to macromolecules, although their study may offer a preferred method of seeking the answer.

6) In a stressed polymeric system one might perhaps expect scission to occur preferentially in the most stressed chains. Would this imply a dependance of scissions on time and of G(scission) on stress during irradiation?

7) Some experimental evidence is available on the nature of the glassy state from the temperature dependance of the radiation-induced process. For methacrylate polymer samples irradiated at several temperatures below the glass temperature the *G* values for scission increase steadily with temperature of irradiation and following a typical Arrhenius plot. Since the required measurements to determine molecular weight must all be carried out above this glass temperature it must be concluded that the temperature at which these differences form is at the temperature of irradiation. One can then surmise that the different scission rates due to temperature may be due to the larger free volume available owing to thermal expansion with temperature. Once the glass temperature is passed there is adequate free space available and a higher temperature does not enhance the *G*(scission) value. Instead another surprising phenomena occurs and some of the polymer evaporates as monomer, to appear elsewhere as repolymerised material. The amount of monomer released in this way, which can be a quite large fraction of the total, indicates that only when irradiated above the glass temperature can this evolution of monomer take place. This imposes a strict limit on the mobility in the glass of low molecular compounds formed during irradiation. It is clear that further work along these lines could provide much information on the nature of the glassy state. In particular one might envisage at least three types of glassy structure; that in which chains are stiff and possibly entangled, but in which radiation would open up the structure allowing more freedom of motion; one similar to the above but which crosslinks on irradiation rendering molecular motion more difficult; and a highly crosslinked system in which the density of true (i.e. permanent) crosslinks allows for no significant flow of molecules between chains. Thus behaviour following irradiation can provide much information on the glassy state.

An interesting observation is that traces of residual monomer trapped in glassy polymer can be largely removed by polymerisation under the influence of a relatively small radiation dose. The question is the manner in which this monomer (<<1%) is present. If as individual and widely separated monomer molecules how does the polymerisation travel through the bulk polymer (the dose involved is too small to permit separate reactions for each molecule); or is the residual monomer retained in pools, too small to be observed, but such that any single radiation event can initiate polymerisation of a complete pool? This may provide one more example where radiation methods might provide an answer to a non-radiation problem. In any case it might appear that individual small molecules are unable to migrate even very slowly through a glassy network.

8) The above observation (7) may be considered in parallel with the observation of electrical breakdown within an irradiated polymeric glass such as PMMA (Plexiglass, Perspex). When irradiated with electrons of suitable energy, an electrical discharge may occur eventually, due to the high density of trapped charge, leaving a highly decorative tree. However, there is no breakdown within a few mm of the surface (except at the point of surface breakdown). It might appear that charge accumulation cannot take place close to the surface, possibly due to leakage through the glass. This might perhaps be ascribed to charge mobility, but a very similar behaviour is seen when irradiated PMMA is heated allowing the gases trapped internally

to form bubbles. Is this due to pools of gaseous products, formed during irradiation and kept under pressure, which are now able to blow apart the weakened polymer to form bubbles, or were the individual molecules kept separate and only now are able to congregate into pools? In any case such bubbles do not form near the surface of the specimen, implying that any gases formed close to the surface can migrate away through the polymer skin and into the surrounding air.

CROSSLINKING AND NETWORK FORMATION

The major practical use of high energy radiation to modify materials has been in the crosslinking of polymers. This can result in a dramatic change in such properties as mechanical behaviour as well as in solubility and swelling. A major factor is the formation of a network structure with highly elastic structure and in some cases a so-called memory effect.

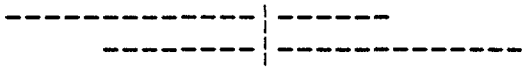
In polymers which crosslink under radiation, chemical bridges are formed between adjacent molecules, which become permanently linked together. These links can be of several types, the simplest being of the H or the T types, referred to as crosslinks and endlinks. Over a very large range of doses the number of such links is generally assumed to be directly proportional to absorbed dose. However, in some instances the validity of this basic assumption should be more fully checked as for example where the effect of unsaturation, polymer morphology and environment could be of importance. However, it has often been confirmed that this simple assumption is valid over a very wide range and the efficiency of the process evalued so that one can trace quantitatively the change in physical properties resulting from the known density of such links. This is best studied in a series of simple linear fully saturated polymers of known average molecular weight such as polydimethylsilicone (PDMS). Similar attempts to relate properties to crosslink density have been performed using chemical methods of crosslinking and these are far less reliable. Once these relations have been analysed in detail in such simple cases, more complex systems can be investigated, as for example polyethylene which is partly crystalline, partly amorphous and flexible, rubber which contains much unsaturation in the main chain, polyvinyl chloride and polypropylene with more complex radiation chemical reactions etc.

The first effect of crosslinking is an increase in the average molecular weight as the number of independent molecules is reduced in proportion to the number of these crosslinks, and their average size increased. If G(crosslink) is the number of crosslinks produced per 100 eV of absorbed energy the number average molecular weight increases from Mn° to M_n due to a dose of r kGy

$$1/M_n = 1/M_{no} + 1.04\times10^{-7} G(\text{crosslinks}).r.$$

For crosslinking there are two crosslinked units per crosslink; G(crosslinked units) = G(crosslinks).

Although radiation can increase the molecular weight considerably, the viscosity is not raised to the same extent since crosslinks can form anywhere along the polymer length, giving branched structures such as



where the extreme distance from one end to another is not greatly enhanced. With the assumption of randon crosslinking one might indeed use a series of such irradiated samples to study the influence of branching on viscosity.

A sudden change occurs at a very well-defined point (gel point) when there is an average of one crosslinked unit per weight average molecule. Once this crosslink density is reached closed loops begin to be formed, theoretically of infinite molecular weight and in three dimensions. Such a network or gel structure is completely different in behaviour from the original or partly crosslinked molecules; if flexible it can have rubberlike properties, and being one molecule it is in theory insoluble, though it may swell. The dose required to reach the gel point is r_g and the density of crosslinking due to any higher dose r is often expressed in terms of a crosslinking coefficient δ related to r and r_g; $\delta = r/r_g$.

Further irradiation ($\delta > 1$) increases the fraction of the initial polymer linked together into a network or gel g, while the remaining soluble fraction s decreases; $s + g = 1$. The relation between the soluble fraction s and dose r depends on the initial average molecular weight and molecular weight distribution. A general formula has been derived relating the sol fraction s to δ and hence to dose r and is found to depend on initial molecular weight distribution. This assumes that these crosslinks occur at random and in proportion to dose. An interesting feature is that whatever the initial molecular weight distribution, network formation first begins with one crosslinked unit per weight average molecule, i.e. at $\delta = 1$.

Simpler formulae are frequently used relating sol fraction s to crosslink coefficient δ (or dose r) for known initial molecular weight distribution. For an initially uniform distribution, with all molecules initially of the same size $s = \exp(-\delta(1-s))$; for an initially random distribution $s+s^{0.5} = 2/\delta$, and for a pseudo random distribution $s = 1/\delta$.

These formulae can be used in a number of ways: to determine radiation efficiency under various conditions; to provide basic information on polymer theory such as swelling and elastic properties; to provide samples of known characteristics such as the gel and sol fractions and the values of M_c; to check on the degree of modification of polymeric products during manufacture with radiation or chemical processes; to determine quantitatively the effect of various additives on radiation-induced reactions including radiation protection and oxidation reactions; to provide a network of known pore size for filtration or medical purposes; to form elastic materials with known degrees of crosslinking or other mechanical properties.

Determination of the effects of radiation in such simple systems can be readily studied quantitatively in a number of ways. The first change i.e. the increase in molecular weight and hence branching up to the gel point is not a very sensitive method since branching or viscosity changes are relatively small. Indeed one might take the opposite approach and use radiation as a means of producing quantitatively such changes when they have to be studied. Determination of the gel point is a very sensitive method and is best achieved by solubility measurements at somewhat higher doses and extrapolation. At even higher doses the solubility decreases in a manner which depends not only on the crosslinking efficiency of radiation, but also on the initial molecular weight distribution. A method often used is to assume an initially random molecular weight distribution for which a plot of $s+s^{0.5}$ against $1/r$ should give a straight line with $s+s^{0.5} = 2$ at the gelation dose r_g, and 0 at $1/r=0$. This simple plot relating soluble fraction to dose provides much practical information on the characteristics of the polymer but has perhaps been overextended into regions where it is not applicable without suitable corrections e.g. for initial molecular weight distribution.

One of the characteristic features of an initially random molecular weight distribution is that its weight average M_w is twice its number average M_n. On irradiation and crosslinking both increase but to differing extents. It is therefore possible to select a virtual dose rv which applied to a random distribution would lead to the initial ratio M_w/M_n. It is therefore often possible to use the popular $s+s^{0.5}$ plot but against $(r_g+r_v)/(r+r_v)$ to obtain a linear plot. Here r_v is a virtual dose which leads to a linear plot and whose difference from 0 is a measure of the departure of the initial molecular weight distribution from a random one.

Beyond the point when solubility has been largely reduced, it becomes possible to use swelling as a good method of determination of crosslinking, but the reaction parameters with solvent must then be ascertained. A further method is the determination of elastic modulus E when the relation with density of crosslinking, characterised by the average molecular weight between successive crosslinks M_c is related to E by a formula analogous to the pressure/volume formula for gases

$$E = 3\ \rho RT/M_c$$

with ρ = density, and with corrections for the soluble fraction and for end effects.

In fact this equation is not entirely satisfactory and a better relation might well be to relate E to the number of effective chains in unit volume of the network irrespective of their dimensions. The validity of this argument can be readily confirmed in a polymer in which radiation causes random scission within the network. This would result in a reduced value of M_c since it is the longer chains which are most likely to scission. If the residual M_c is reduced E should increase and this is obviously incorrect; chain scission cannot cause an increased elastic modulus.

A further method of analysis, as yet not widely adopted, is the use of pulsed NMR to determine not chemical structure, a well-established and widely used technique of chemical analysis, but morphology and mobility of macromolecular chains. In this method the spin-spin decay is plotted against time. For a lower-molecular weight flexible polymer a simple exponential decay is observed with characteristic $T2$. Spin concentration $S = So.\exp(-t/T2)$. $T2$ is found to depend on molecular weight, (T_2^2 1/M. as well as on temperature and concentration in solvent where present and appears to be closely related to vicosity in the system. With a partially crosslinked system a sum of two exponentials is observed and these are determined by the network g and non-network s fractions as well as by M_c.

For much higher molecular weight flexible polymer a double exponential is already found with a non-crosslinked i.e. completely soluble polymer. This is ascribed to an entangled system in which the polymeric molecules maintain a kinetic network structure with a sufficient density of forming and reforming entanglements to constitute a dynamic network. It may be assumed that the lifetime of such entanglements is greater than the measurement time of the NMR equipment (less than 1s) so that they appear as crosslinks. As the temperature is raised their lifetime decreases as does the effective fraction of the entangled network. This relatively simple method of determining number and temperature dependence of entanglements promises a quantitative method of accounting for creep in polymeric systems. This NMR method also permits the assessment of crystallisation rates and of amorphous fraction and their dependence on temperature and solvent. It may also lead to the assessment of such properties as adhesion and degree of cure.

Unfortunately this pulsed NMR technique has not been fully developed, although it should also be applicable to biological systems, where it appears to offer a promising method of assessing radiation effects in terms of the resultant morphological and structural changes due to very minor chemical changes resulting from irradiation.

POLYMERISATION

The use of radiation to initiate polymerisation has led to a considerable amount of very detailed and effective research, but with far less effective applications, despite the considerable advantages that this route offers. No chemical initiating additive is required, whose activity is strongly dependent on temperature and state etc. and which can leave unwelcome residues. With radiation initiation the reaction can be initiated over an enormous range of radiation intensities and correspondingly high rates of initiation and which can be largely independent of temperature. Where the reaction proceeds via a radical mechanism, it often progresses as the root of the radiation intensity, since propagation ceases when two growing chains, each initiated by a radiation-induced event and terminated by a radical, meet and propagation ceases. Under such conditions control of chain length is determined primarily by radiation intensity, while the number of molecular chains is related directly to total dose. However, chain transfer can be

an additional factor. Nevertheless, in many instances a less direct dependence on dose rate is found, and details of the kinetics of the reactions resulting from radiation initiation (and possibly subsequent reactions) under various conditions could be of interest.

Ionic polymerisation is also possible though here the kinetics may be different and published results show that the yield is proportional to total dose but not intensity. The ionic reaction in such cases is best ascribed to the trapping of an electron in the vicinity of its parent monomer until recaptured; thus each polymerisation chain proceeds independently of the others.

Polymerisation can also occur at low temperatures, in the solid state and still at high efficiency. It can also occur within another solid system which it can serve to stabilise without involving the formation of an insoluble network as in radiation induced curing. Under these conditions it may prove economic to use relatively cheap monomers.

One of the difficulties encountered with polymers obtained by conventional chemical catalyst initiation is that a small amount of monomer remains unreactive within the system and interferes with the subsequent use made of the polymer. One does not want to envisage the constant reduction in performance due to what may effectively be a trace of highly compatible monomer, which may also evaporate very slowly leading to some extent in instability of performance. It was discovered that a relatively small radiation dose could reduce this residual monomer. The cause of this marked reduction at these low doses is not known. Various explanations have been suggested: energy transfer of the energy absorbed at one point of another until it initiates further polymerisation; however, this would raise one difficulty in that each initiating species energised in this way could only bind one monomer unit if this is dispersed at low concentration in the vicinity of each primary radiation-induced reaction. A second possibility is that after each such reaction the residual radical is not destroyed but migrates further to initiate more of such reaction. A third possibility is that the residual monomer agglomerates in pools where any single initiation by radiation will cause widespread polymerisation since for such a radical process two events would be needed to complete the process; in the absence of this pair (or another even number) the polymerisation process must continue. This radiation reaction has been envisaged as a method of reducing residual monomer in polymer stocks where these are produced by conventional chemical initiation.

Various other possible radiation-induced reactions may be envisaged such as a radiation dose delivered in two or more parts at very different intensities allowing a geometrical distribution of polymer of various parameters throughout a composite structure. Radiation curing of highly reactive, low molecular weight compounds may be considered as a special form of polymerisation.

GRAFT POLYMERS

Much research effort has been devoted to the study of radiation-induced grafting of sidechains formed by monomer B onto a very dissimilar polymer chain A, but in spite of its considerable promise of a simple method of binding two diverse systems together, this has not led to any industrial production comparable in size to that obtained from crosslinking of available polymeric chains. This lack is not due to the technical difficulties but rather to insufficient demand for the grafts already obtained, and even more to insufficient knowledge of what new problems have arisen and might be solved with this method. Perhaps scientists with experience in this field and with initiative might be encouraged to maintain closer contacts with industrial concerns and search for new and unsuspected needs which might be met with these new possibilities with which they are more familiar.

Several methods have been developed; simultaneous irradiation of polymer A and monomer B, alone or in the presence of a solvent; preirradiation of polymer, relying on trapped species such as radicals to initiate polymerisation and grafting when subsequently immersed in monomer; and the peroxide route when oxygen is present. In this last method irradiation of the polymer P forms radicals which combine with oxygen to produce relatively stable hydroperoxides which can subsequently be broken by heating or uv

$$P. \quad PO_2 \rightarrow PO. + .OH$$

$$PO. + M \rightarrow POM.$$

and $$.OH + M \rightarrow HOM.$$ homopolymer

The result is both graft and homopolymer but the latter is not always desirable. Its presence is largely avoided by the presence of certain metallic salts such Mohr's or ferrous salt.

$$POOH + Fe^{++} \rightarrow PO. + OH^{-} + FE^{+++}$$

The formation of undesirable homopolymer can also be avoided by introducing the monomer in the form of a gas. In radiation grafting one is faced with competition between polymerisation and grafting and by a suitable choice the latter may be enhanced. Additives such as sulphuric acid and inorganic salts have been introduced to enhance the grafting.

Although grafting is generally taken to proceed via radicals, ionic reactions may also be involved under certain conditions. In this case the environment may be of the utmost importance as it is in polymerisation at low temperature. The rate of grafting can also be enhanced by the use of certain additives such as mineral acid, or polyfunctional additives at sufficiently low concentration to avoid crosslinking and network formation. With these various techniques a vast range of products can be formed but may be difficult to control in the greatest detail; the same difficulty is to be expected in chemical techniques of grafting, but the use of radiation to initiate the reaction has a great advantage in that it depends

little on factors such as temperature or dose rate, which can therefore be used to control other parameters such as chain length and possibly location.

A number of applications have been developed. The backbone structure is derived from the base polymer and this may be chosen to be relatively inert chemically; the side-chain graft can then serve independently for its chemical reactivity. Various types of membranes have been produced as in battery separators and membranes for chemical separation purposes. Grafted films have also been available for waste water treatment.

Grafting of acrylic acid to polyethylene has received much attention; when grafted to celluloses it results in excellent water-absorbing properties for use in kitchens, chemistry and agriculture. Surface grafting can modify surface properties such as improved adhesion, binding, modified compatibility, catalyst support systems etc. Grafted systems have also been envisaged in some advanced forms of printing, microlithography, and in surface treatment of textiles.

Much effort has been devoted to the irradiation of wood into which monomer has penetrated. This could result in both grafting and homopolymerisation within the free volume. Thus the introduction of methacrylate monomer (methyl, butyl) into a variety of woods has greatly decreased water uptake under wet or moist conditions as is shown for example by the far smaller decrease in resistivity.

The use of this grafting technique is being actively followed in biomedical applications, where diverse sidegroups may be grafted onto a backbone, and then allowed to interact with diverse bioactive materials to form immobilized biomolecules. Examples are enzymes, antibodies and antigens, drugs; aminoacids, antithromogenic agents and even amino-acids and DNA. Radiation grafted microbead carriers have also been produced having greatly improved binding capacity for ligands and biomolecules used in biomedical applications.

A graft of styrene onto certain types of polypropylene followed by sulfonation is envisaged as being the base of a far more effective absorbent for the removal of toxic gases.

IRRADIATION OF SOLUTIONS

Much research effort has been devoted to the irradiation of solutions, but this has been largely concerned with study of the interaction of the species both in solvent and in solute. The observed effects can be ascribed to the species such as radicals formed directly by radiation, but also to those formed indirectly by such effects as energy transfer between species before a chemically reactive species is formed. Of particular interest are the reactions of irradiated water as solvent. On the more applied side the interest has been largely concerned with the irradiaton of hydrophilic polymers dissolved in water, perhaps with the addition of a very small amount of an additive.

The basic reactions were investigated some forty years ago and showed that in aqueous polymer solutions, crosslinking occurs at increasingly lower doses as the concentration is reduced i.e. the further the molecules are apart. Typically the dose for gelation and network structure can be reduced from a few Mrads or tens of kGy in pure polymer to well below one-tenth of this figure as the polymer concentration is lowered to about 1%. This leaves a greatly swollen network structure of only a few percent polymer network. However, this should not be considered as an increased yield or higher total *G* value, since the total amount of crosslinked polymer per *g* of irradiated solution is correspondingly reduced. One is transferring energy absorbed in water via reactive species to a much smaller amount of polymer.

A remarkable change occurs at a polymer concentration of less than about 1% when no crosslinking appears to take place and no swollen polymer network is formed. The explanation is that crosslinks can occur between units of adjacent polymer molecules but also between units within the same macromolecule. At low concentrations the latter predominates and an increasingly tight network is formed, consisting effectively of a swollen and extremely fine separate powder, i.e. a microgel possibly of molecular dimensions. One could therefore use this technique for modification of polymeric but also of biopolymeric systems. It can impart information on molecular configuration in solutions and the effect of conditions such as pH, nature of solvent, of additives, of sidegroups and even of molecular weight can thereby be studied in a relatively simple manner by measuring the doses at which this apparent change from solution to gel or to microgel takes place. A further extension might be to form this microgel at a very low concentration and then by reducing the water content link these microgel particles together into a more open structure with a further radiation dose. This would produce a new structure of a more complex character.

The major practical use to date of such macrogel or swollen network has been for hydrophilic polymers as a sterile and transparent bandage. This has several advantages over existing opaque products; it allows the wound to be examined without removal, does not adhere and is sterile when applied with no further treatment. The pore size is determined by the radiation dose, which can therefore be chosen to regulate degree of swelling and the diffusion rate of drugs or other materials. Such bandages have been tested in hospitals with very promising results.

In practice the hydrophilic polymer is dissolved in water, possibly with very minor addition of other additives, and sealed into a polyethylene bag. This is then irradiated in a suitably shaped container so that any desired final product can be determined during radiation, at the same time as pore size. In practice a dose of 25 kGy can be chosen since this ensures sterility for an indefinite period until the bag is opened for use. It is even possible to commence with a hydrophilic monomer in water, this ensures that all stages, polymerisation, crosslinking into a network of desired shape and sterilisation can occur in a single step of irradiation.

One can visualise this type of reaction and product becoming of widespread use for other medical and pharmacological purposes. It combines cheapness, sterility, considerable flexibility and control of shape as well as pore size and diffusion rate. An entirely different group of applications may result from the crosslinked microgel, which can consist of an extremely fine powder, which can be swollen to a very large extent (perhaps several hundred times), while remaining completely soluble. Pore size is simply determined by dose and can regulate drug uptake and release. Other uses for the macroscopic hydrophilic gel of predetermined pore size may also be expected to develop as the ability to produce such materials simply and under accurately controlled conditions is more widely appreciated.

RADIATION CURE OF POLYESTERS

The simple process of crosslinking involves a reaction between adjacent polymer chains, but without involving any further reaction on other adjacent molecules. Each crosslink takes place independently of all others. However, a very different situation may arise when the link of molecule A to molecule B increases the probability of A or B becoming linked further to C and thereby to D, E etc. A very considerable change could then result not only in the sequence of reactions but also in the nature of the final product. The promise of this different pattern of behaviour is most easily noted in the extensive research and production activity associated with curing and adhesives.

In the curing of polymeric formulations, radiation only intervenes in the initial stage, to form a link but one which when formed, can act as an initiator for a chain of further links formed chemically. This further sequence is in many respects akin to a polymerisation reaction initiated by radiation but passing through polymer molecules. To achieve these further chemical reactions, appropriate chemical structures must be available at each step, and this is best achieved by the presence of unsaturated groups. These unsaturated and reactive groups may be present in the original polymer molecules themselves, or be introduced by suitable mixed polymers or more conveniently low molecular weight multifunctional additives.

$$A \quad A^{\cdot}; \quad A^{\cdot} + B \rightarrow AB^{\cdot}; \quad AB^{\cdot} + C \rightarrow ABC^{\cdot} \ \ldots \text{ or}$$

$$A \quad A^{\cdot}; \quad A^{\cdot} + M \rightarrow AM^{\cdot}; \quad AM^{\cdot} + B \rightarrow AMB^{\cdot} : AMB^{\cdot} + M^{\cdot} \rightarrow AMBM^{\cdot} \quad \text{etc}$$

or with a multifunctional species (Monomer or Polymer)

$$A^{\cdot} + M \rightarrow AM^{\cdot} \qquad AM^{\cdot} + B \rightarrow AMB \text{ and also } AMB + C + D \rightarrow AMB$$

Where one is linking together a series of polymeric molecules by the addition of such low molecular unsaturated molecules, much depends on the degree of unsaturation. With only one such reactive group per molecule, each can only result in one link and will require one radiation event. Unless there is further propagation the statistics will not differ fundamentally

from random crosslinking discussed above. A completely different set of statistics applies when polyunsaturated or multifunctional additives are present. The behaviour of such composite systems involves two quite distinct stages; (i) the stage where polymer molecules A B C D ... are linked into a much longer sequence which is essentially a very high molecular weight, highly branched system and (ii) the linking of these extensive molecules together into a three-dimensional network. A full statistical analysis of its formation does not appear to have been published.

This process of forming a network is highly efficient and granted the presence of adequate polyfunctionality in each monomer requires very little initiation to form a highly crosslinked network, very akin to a glass. The degree of crosslinking can no longer be deduced from its highly elastic deformation but can still be assessed in various ways including its hardness and soluble fraction.

As an example the radiation effects in an unsaturated polyester can be quoted. UP-K has a molecular weight of 1000 and an unsaturation of 0.2 moles/100g (2 per molecule). This may be compared with a fully saturated alkane of similar molecular weight which with random crosslinking would require about 7000 kGy to reach the gel point. The gelation dose for this unsaturated polyester is not given but it reaches a hardness value of about 5% at a dose of 200 kGy and this must be well beyond some simple form of network structure. With the same polyester and a highly unsaturated monomer additive (trimethylolpropane-triacrylate molecular mass 300 and 3 double bonds per molecule) mixed at 50/50 the gelation dose is approximately 20 kGy corresponding to a G value of about 400, if one uses the conventional formula for random crosslinking, and also a hardness of 60% of maximum at a dose as low as 75 kGy. With related additives to the polyester but of slightly lower average unsaturation the required doses may be doubled. This simple example is intended to show how sensitive such systems are to dose and degree of unsaturation.

The following points of great relevance should be considered.

(1) The dose required to form this dense crosslink density is greatly reduced as compared with random crosslinking. For example a low molecular weight unsaturated oligomer can be almost fully cured at a dose of 10 kGy. A linear alkane of the same molecular weight would require a dose hundreds of times greater.

(2) The molecules with multiple functionality may be present either in the polymer or as an additive which is bifunctional or higher, as in certain acrylates of high functionality.

(3) The ready formation of a very highly crosslinked network presents a glassy type of network of low M_c and pore size and consequent low porosity. Much of the additive will remain at least partly un-reacted and may have to be removed in some way, as by further radiation.

(4) This type of reaction can be readily obtained in thin films, and can also be initiated by ultraviolet light. Such photochemical reactions have certain advantages and disadvantages as compared with fast electron beam initiation, and both are utilised in different applications.

Ultra-violet sources do not require strong shielding and are available in small, relatively cheap installations. The penetration of u.v is limited and suitable additives or photochromes must be present. It cannot be used in the presence of carbon black, of heavy pigment coatings or many reinforcing agents acting as fillers. The photosensitisers needed may be expensive and will not always be 100% utilised.

To be economically feasible high energy radiation sources must be powerful and correspondingly expensive to install. A conventionally powerful (about 200-400 kV) machine with its shielding can be installed on a factory floor and there cure kilometers of strip or film per hour. Once installed, the electrical power costs are low. Apart from a multifunctional additive for crosslinking purposes, no specially sensitive additive is needed. It can be used for opaque objects and doses can be increased to reduce residual additives. However, oxygen may intervene in the reaction especiallly on the specimen surface. Problems of dosimetry and of familiarity with high-energy radiation must be overcome. It can be used to modify continuous strips of materials in various ways, from the roll, as curtain coating, by spray coating and by extrusion coating. No solvent need be applied thereby avoiding contamination of the environment.

Applications in wood can involve impregnation, filling and surface coating; this can impart increased strength and hardness, abrasion resistance and resistance to penetration and attack by fluids. Surfaces can also be improved, and if required decorated. In Central Europe for example radiation is used in the production of electron beam coated cement-bound chipboard panels for building purposes. The surface properties and decorative interest of paper and plastic surfaces can be readily improved by radiation curables; these can include the use of thin plastic films as overcoats on containers, and for surface metallising. The surface of glasses and ceramics can also be modified in a number of ways as in mirrored, decorative or transparent protective surfaces, or for surfaces on glass or other fiber communication filaments and cables.

The coating of metal surfaces for decoration, chemical or abrasion resistance is also being developed. The curing of paints on metal sheets and framed objects in the automobile industry promised to represent a major step forward, eliminating the passage through long heating tunnels, but owing to an unfortunate accident, was abandoned for a long period and is now being applied to smaller components. One of the aspects of radiation curing of paints is that no solvent is needed nor need it be evaporated or otherwise disposed of. It is quite likely that entirely new chemical formulations might be developed, possibly with other improved properties. Here of course u.v. light would be unsuitable for an adequate cure.

Numerous other applications are being developed into large-scale industrial processes. Examples are the surface coatings and binding of magnetic components and composites. For example information is available on improved peel strength and higher peel temperature in synthetic rubber resin adhesives; this is to be expected since temperature plays very little role in radiation curing reactions which can therefore be promoted to a higher degree.

Because of its very special properties one can envisage marked increases in the use of radiation in the adhesives industries. New types of bonding reactions as well as new materials and novel methods of application may be developed, not amenable to existing techniques.

It appears to the writer that one of the main difficulties is to ascertain where new types of needs are present in industry or elsewhere. Some of these may be known to industrial leaders, but they may not be familiar with the unusual advantages which can be found in radiation technology. Perhaps a more successful approach is for the more open-minded scientists familiar with past radiation application successes to become more acquainted with industrial needs outside their scientific specialisation.

FOOD IRRADIATION

Research into the irradiation of food to improve some property represents one of the earliest attempted applications of large radiation sources, and some of its advantages in terms of health are manifest. One may therefore query the massive objections to its use in practice, at a time when the parallel application to medical sterilisation has been so widely accepted. In fact the major objections are not usually of a scientific nature, although to enhance their impact on the credulous public, this impression is often given.

The problem is psychological rather than physical and represents not only the widespread lack of basic scientific knowledge in our modern so-called scientific age, but even more the opposition by certain groups to the spreading of any such information, which they appear to resent. This attitude is not confined to an anti-food radiation lobby but here it finds a suitable target for its anti-scientific views. To some extent the scientific community is partly to blame for this situation as it lives so passively in its own world, only emerging briefly and when essential to confront a direct challenge and major misrepresentation. One may perhaps consider this as another example of the need to bring the scientific approach more closely into the general outlook of the wider community.

Much play is made of possible changes in chemical structure of foods exposed to a sterilising dose. Although these are very minute (or they could be used for confirmation of radiation treatment) it is claimed that they might nevertheless be dangerous. I have confirmed that no correspondingly detailed tests have been carried out on new dishes obtained by cooking alone although the chemical changes are unknown and far more drastic. One is entitled to ask members of the anti-radiation

lobby not to eat cooked foods until they have been checked for safety to the same extent as they demand for irradiated foods.

The more specific details on food irradiation will be dealt with separately. However, the possibly considerable advantages of food irradiation in a world likely to suffer increasingly from widespread food famine in one or two generations require a very vigorous and widespread campaign to familiarise people with the meaning and potentially widespread benefits of radiation treatment in its various forms and of potential dangers which it can meet. In particular it should emphasise the difference between irradiated and radioactive, the presence of natural radioactivity in the world in which we live and the benefits which we enjoy from well-controlled uses of radiation as in medical treatment and sterilisation.

CONCLUSIONS

One may envisage the study and use of high energy radiation from a number of points of view. Considering only its beneficial uses in industry, agriculture and medicine, (and excluding nuclear matters and uses for medical examination and treatment), one has seen emerging and becoming well-established two major applications. Both involve extremely small chemical changes applied to macromolecules yet resulting in new systems with very considerable physical and biological advantages. As more information becomes available, new but related developments mature. Here we may expect steady progress in a number of directions such as higher radiation resistant and fire-retardant cables, new composite materials and ultimately polymers of higher strength. The application of controlled electron beam intensity for scanning across specimens offers differential effects and a form of composite three-dimensional structure difficult to achieve in other ways. The production of foamed materials with controlled spore size and the production of grafted films for chemical control such as catalysts.

At the same time we can visualise radiation being used to provide samples of known characteristics, which can provide the basis of further scientific and engineering data of wide interest in many aspects of polymer science and microbiology.

We also expect to see further progress in understanding the basic mechanisms involved in the irradiation of organic systems and elucidation of reactions such as those often referred to as energy transfer or radical migration etc. However, it is now becoming clear that many of the apparently simplest radiation-induced reactions are in fact far more complex.

It is my personal view that in some irradiated organic systems, morphology can play an extremely important role in their eventual behaviour under radiation. Even in the case of polyethylene there are marked differences according to the form of crystalline chain-folded structure; its previous history can have considerable influence.

Many close relationships have been found between the radiation effects in synthetic and biological polymers. The

importance of such factors as morphology and mobility already seen in simpler polymers must also hold true for biopolymers. Extension of this type of research (possibly using pulsed NMR T_2 methods) to other polymeric systems and especially to biopolymers might be expected to open wide new vistas.

The conductivity and light emission from irradiated organics can be expected to advance rapidly and throw far more light on the mechanism of charge trapping and subsequent electrical breakdown. Also further work on semiconductor behaviour could have both theoretical and practical interest.

Progress in other fields, especially food irradiation, has often been regrettably slow for several reasons, a major one being a public reaction to the term radiation, which has been partly confused with nuclear weapons and unsafe nuclear reactors. Here it would appear that some form of better public understanding is required. Another is the lack of familiarity of much industrial leadership with the possibilities and advantages of radiation processes, and it must be said, often with poor business planning, directed to the immediate future return rather to longer-term investment. One would be amused to imagine the proposals submitted by Michael Faraday and Clerk Maxwell searching for funds to support their researches under present conditions. To this must sometimes be added the narrow outlook of some radiation scientists, mentally as well as physically confined to their laboratory bench. It should be the novel aspects of radiation processes which offer the major challenge.

During the last forty years, many conferences have taken place throughout the world on the subject of radiation applications. These are largely filled by scientists presenting their most recent results and measurements under conditions where the implications of their work cannot be followed or discussed. Reviews of part of the subject by leading experts at these conferences have been most popular. One would like to see meetings at which not only is new progress reported, but also the opportunity furnished for joint presentation of problems still unsolved. This might spark off a vigorous discussion, the presentation of unsuspected but relevant data, and perhaps inspire new lines of research amongst some new and budding scientists not yet fully immersed in existing matters.

An important feature of future progress on an industrial scale is the provision of powerful radiation sources at reduced cost. If necessary these could be somewhat less accurate and precise than present-day machines if the capital cost could be greatly reduced. They could be used in areas where this relatively high precision is not fully justified. Irradiation of wastes such as sewage and effluents is one example.

Competition in certain areas must be envisaged e.g. from ultraviolet sources, and here the cost of equipment and installation will be vital.

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HIGH LET RADIATION CHEMISTRY

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Abstract

LET effects are widely discussed in connection with radiation induced physical and chemical interactions with matter. Earlier works on LET effects of polymers through product analysis are introduced. Then, spatial distribution of radicals, generated by various kinds of radiations in organic compounds, is summarized. Finally, several new recent results on LET effects, like transient phenomena, are described and discussed. Helium gas, water, KCN, and organic compounds, including biological molecules and polymers, are cited as the target materials in gaseous, liquid and solid phases. High LET radiation is characterized by high levels of excitation, nuclear recoil processes and high densities of excitation. This gives rise to very specific chemical reactions in target materials. It is emphasized that high LET radiation chemistry is a fascinating new field of science.

1. Introduction

Linear energy transfer (LET) is defined by the following formula:

$$LET = -\left(\frac{dE}{d\chi}\right) = (M, \varepsilon, E)$$

This is energy deposition of charged particles with energy of E to matter along the trajectory axis χ, where M is the mass of the charged particle and ε is the number of charges of the particle. This is divided into the following three terms:

$$-\left(\frac{dE}{d\chi}\right) = -\left(\frac{dE}{d\chi}\right)_E + -\left(\frac{dE}{d\chi}\right)_I + -\left(\frac{dE}{d\chi}\right)_P$$

E - Elastic, I - Inelastic, P - Emission

The interaction of high LET charged particles with matter is characterized as follows:

A. Formation of highly excited states through super-excitation, multi-ionization, and inner-shell ionization,
B. Effective generation of recoil atoms,

In general, higher LET radiation provides both higher excited states and higher density of excitation in material to be irradiated.

Specific radiation chemical effects induced by energetic charged particles are based upon the characteristic aspects mentioned above.

2. Experimental

In order to study the LET effect, various experimental methods can be used. Especially, the electron spin resonance method is useful to know spatial distribution of active species in target material generated by high energy particles. By irradiation of material at a very low temperature, transient species are freezed at such temperatures after irradiation. Heterogeneous spatial distribution can be measured by this method.

Pulse radiolysis is a powerful tool to study early processes. Photon counting is also a very useful and powerful method to investigate the transient phenomena.

Experimental procedures could be summarized:

Time dependent phenomena	Pulse radiolysis and Photon counting
Steady state phenomena	Under irradiation
Permanent changes	Product analysis

Through the experiments, spatial distribution of either transient species or chemical products can be determined.

In order to study the LET effect, incident energy of charged particles can be changed for a fixed thickness of target, in other words: at a fixed position or location along the track. This may be called "energy dependent LET" study. On the other hand, under a fixed incident energy of the charged particle, radiation induced phenomena could be measured along the beam track as a function of distance from the surface. This may be called "site or location dependent LET" study.

Interesting examples will be described in this review.

3. LET Studies by Product Analysis

A series of papers concerning the LET effect have been published during the past 20 years. In the early stage, the experiments had been carried out using nuclear reactors. Some had been done by using ion beams from cyclotron machines.

Since about 10 years ago, Van de Graaff machines, Tandem accelerators and cyclotrons have been used for these experiments. Some examples are shown in Table 1.

Both G-values of crosslinking G(X) and chain scission G(S) for polystyrene were found to be 10 times higher for fast neutron irradiation than those for irradiation of either gamma or energetic electrons. Spatial distribution of the crosslinking and chain scission have been estimated to be very heterogeneous for the fast neutron irradiation, compared with gamma or electron irradiation. G(S) for PMMA decreases with increasing LET. The spatial distribution of chain scission is also more heretogeneous for fast neutron irradiation than for gamma or electron irradiation in the case of PMMA.

4. Spatial Distribution of Radicals

A series of organic compounds were irradiated with fast neutrons by using a fast neutron source reactor "Yayoi" at the University of Tokyo. Local concentration or mean distance of radicals formed at low temperatures was estimated from the electron spin resonance experiments (14).

These results are summarized in Table 2.

5. Transient Penomena

5.1 Electron pulse radiolysis of H_2O has been carried out using an S-band electron linear accelerator at the University of Tokyo in Tokai (15). Decay of solvated electrons was measured at elevated temperatures with different intensities of electron pulse (dose). The decay depends upon both the initial dose and temperature. The experimental results are shown in Fig. 1.

Table 1 LET Studies

Compounds	Radiation Source	References
Polystyrene	Nuclear Reactor, Van de Graaff	1,2
Polymethylmethacrylate	Nuclear Reactor, Cyclotron	1,3
H_2O	Nuclear Reactor, Van de Graaff, Cyclotron	4
Benzene	Van de Graaff	5
Aliphatic ketones	Cyclotron	6
Eicosane	Cyclotron, Synchrotron	7,8
Acrylonitrile	Nuclear Reactor, Synchrotron	9
Acrylonitrile	Nuclear Reactor	10
Propylene-tetrafluoroethylene	Nuclear Reactor	11
Ethylene-Propylene Rubber	Cyclotron, Nuclear Reactor	12
Polyethylene	Cyclotron H^+, Nuclear Reactor	11,12
Polypropylene	Cyclotron H^+	12
Ethylene-vinylacetate copolymer	Cyclotron H^+	12
Ethylene-tetrafluoroethylene-copolymer	Cyclotron H^+	12
Nylon 6	Cyclotron H^+	12
PET	Cyclotron H^+	12
PES	Cyclotron H^+	12
U-PS	Cyclotron H^+	12
U-Polymer	Cyclotron H^+	12
Various compounds including organic molecules		13

Table 2

Spatial Distribution of Radicals

Compounds	Radiation Source	Local Concentration or Mean Separation
Alanine	nf/γ	1.0
Phenylalanine	nf/γ	1.6
Histidine	nf/γ	1.7
Monosodium Glutamate	nf/γ	1.4
Aspartic Acid	nf/γ	1.6
Malonic Acid	nf/γ	1.9
Nicotinic Acid	nf/γ	2.7
PMMA	nf/γ	2.5
n-Eicosane	H^+, 60 MeV	1.8
n-Eicosane	H^+, 85 MeV at 77K	1.6 Å

The decay curve of lag is a single line until tc (which depends on temperature) independent of the initial dose, and then diverges depending on the initial dose. The higher the dose, the faster the decay after tc. The higher the temperature, the shorter the time period up to tc.

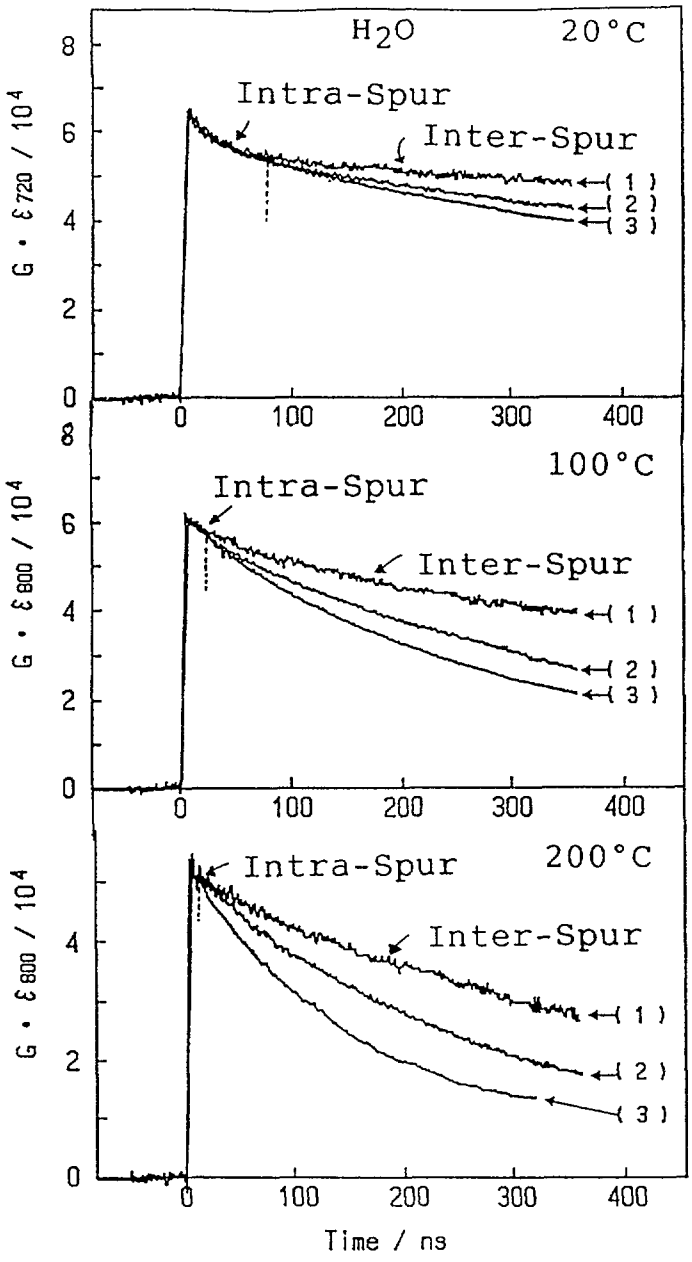

Fig. 1 Decay of Solvated Electrons in H_2O at Various Temperatures (Shiraishi et al)

This is indicating that spurs formed during the pulse irradiation are isolated from each other and do not overlap until tc, then start to overlap by diffusion from the tc. Therefore, intra-spur phenomena could be distinguished from inter-spur ones in these experiments.

5.2 In proton pulse radiolysis of a thin film (0.5 μm) of polystyrene, transient emission around 328, due to formation of excimer can be observed. The results are shown in Fig. 2 (16).

For a higher current of H^+ (0.6 MeV), no change in the intensity is observed during the measurement. This indicates that the tracks are isolated from each other at a low dose rate during the period of experiments, and the tracks become overlapped during measurements at a high dose rate under the experimental conditions. Excimer is considered to be quenched by active species formed by irradiation. For a higher current experiment, the density of tracks becomes higher. Therefore, the time for overlapping

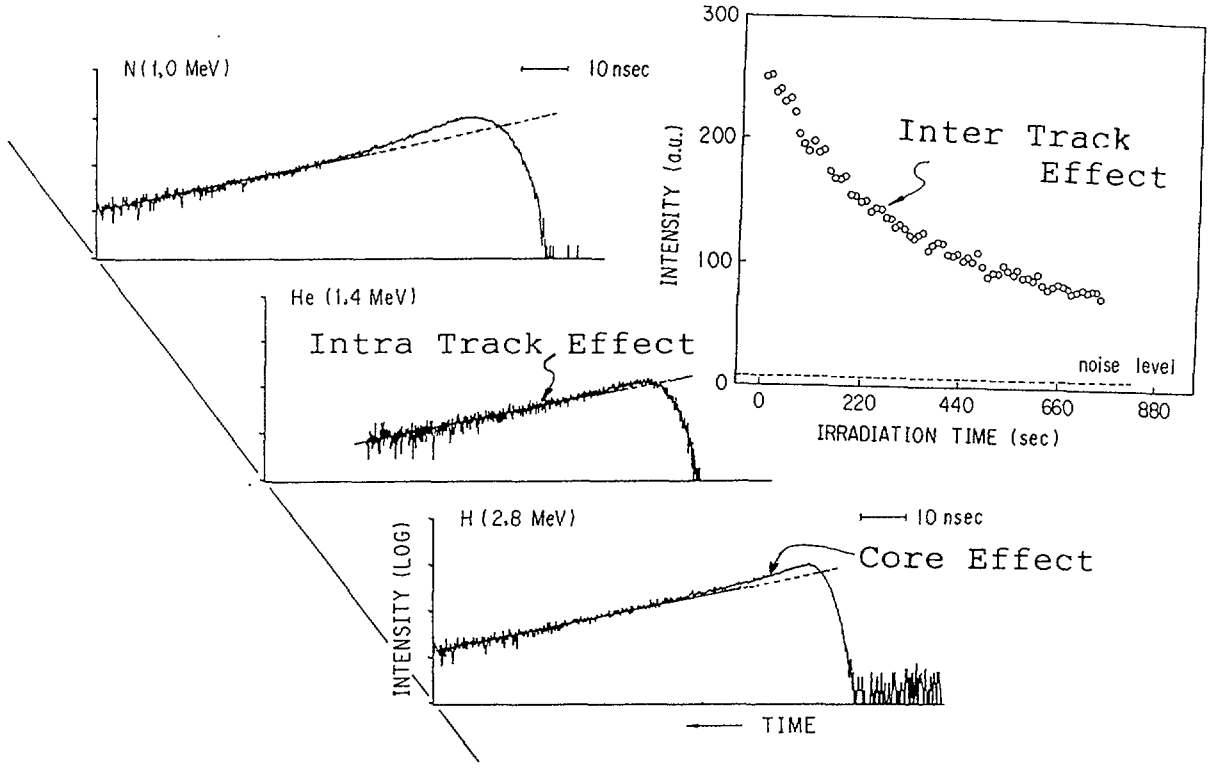

Fig. 2 Excimer Formation and Decay in Polystyrene by Various Ion Beams

of the tracks by diffusion becomes shorter and comparable with that of the quenching. As a result, the effect of the inter-track interaction becomes significant for the quenching process under a higher dose rate. Through these experimental results, intra-track phenomena could be distinguished from inter-track ones.

Initial decay of emission in the intra-track at a low dose rate depends on the kinds of charged particles (1.0 MeV N^+ , 1.4 MeV He^+ , and 2.8 MeV H^+). The higher the LET, the faster the decay. It is suggested from those results that quenching of the excimer occurs favorably at a higher density of excitation in a track.

5.3 Pulse radiolysis of saturated linear hydrocarbons in liquid phase is also interesting (17).

Lifetimes of excimer in n-dodecane is shown in Fig. 3. It is evident from the figure that the lifetime decreases with increasing LET. This may be due to quenching of excimer by excited species formed in the track. The higher the excitation density, the more effective the quenching.

5.4 When PPO is dissolved in solvent, energy or charge transfer from the solvent to the solute occurs. Then, emission from PPO* is observed. Lifetime profiles of PPO* in benzene and cyclohexane are shown in Figs. 4 and 5 respectively (18).

Gamma-rays from Co-60 and alpha-particles from Californium have been used as the radiation sources. The lifetime spectra were obtained by the photon counting method.

In cyclohexane, PPO* is formed through energy and charge transfer from the solvent. As the singlet excited state C_6H_{12} * is quenched by transient species such as C_6H_{11} in the track, the fast decay component shown in the figure appears for the He^{2+} ion irradiation. On the other hand, in benzene a slow decay component appears for He^{2+} ion irradiation, in spite of the fact that no slow component appears for gamma-irradiation. This is due to fast formation of triplet benzene at a high yield, because, after energy transfer from triplet benzene molecule to PPO, a delayed formation of PPO* (singlet) from PPO*(triplet)-PPO*(triplet) annihilation in the track occurs.

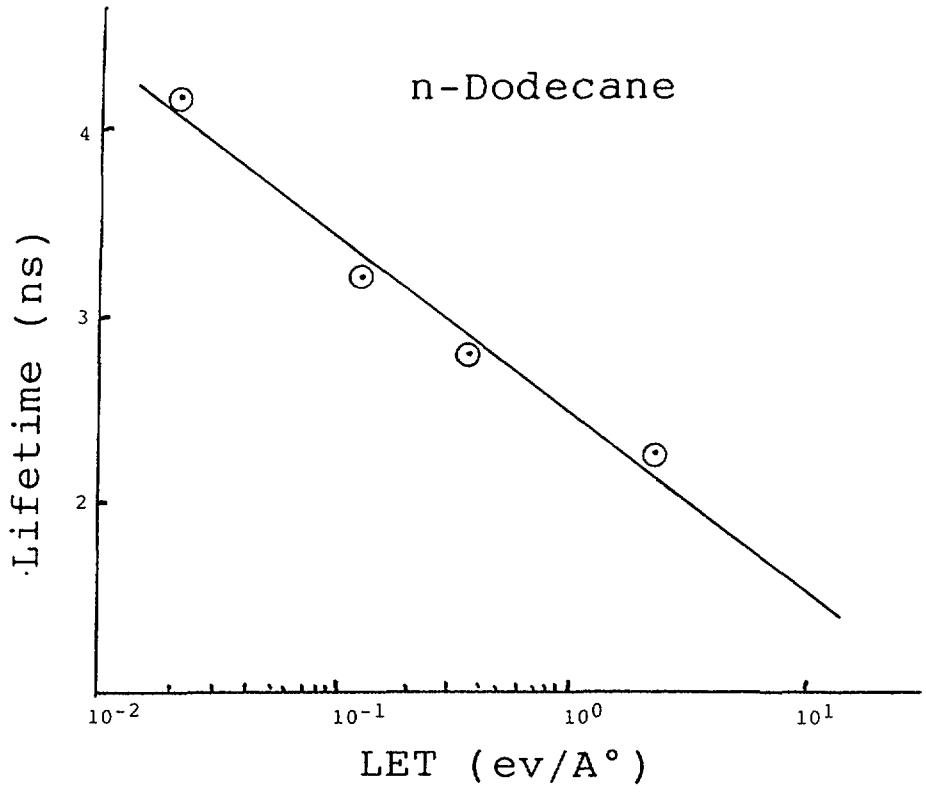

Fig. 3 L.E.T. Dependence of Lifetime of Singlet Excited State

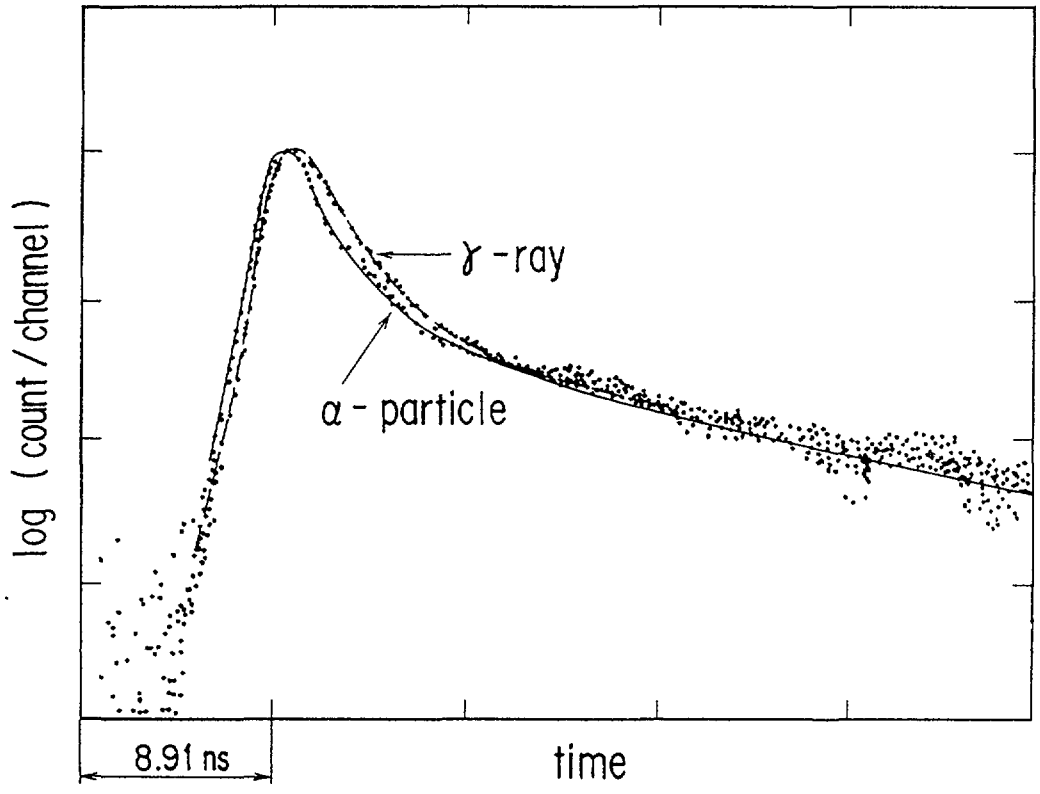

Fig. 4 Decay of PPO Singlet State in Cyclohexane

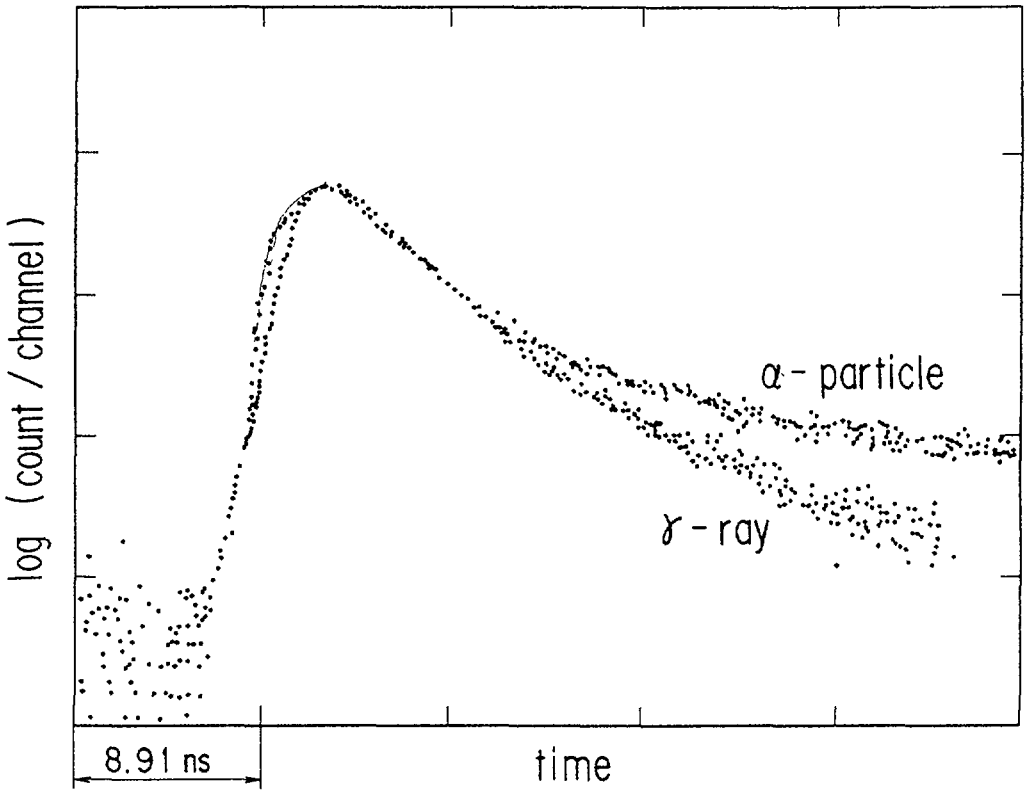

Fig. 5 Decay of PPC Singlet State in Benzene

In conclusion, both fast decay of PPO* in C_6H_{12} and slow decay of PPO* in C_6H_6 result from high density excitation in the track of He^{2+}.

5.5 New emission bands have been observed by high density excitation of dense helium gas or liquid helium. Nitrogen ions N^+(4 MeV/amu) were used for irradiation (19).

The two new bands which can be formed only by high density excitation have been tentatively assigned to be $(He^*_2)_3$ and $(He^*_2)_4$, respectively. They are effectively formed just after the Bragg peak.

5.6 Very effective crosslinking of polystyrene thin films by ion beams has been observed recently by the authors (20).

G values of crosslinking is shown as a function of LET in Fig. 6. It is quite clear from the figure that polystyrene, which is a typical aromatic polymer, is quite sensitive to ion beam irradiation, contrary to gamma or electron irradiation. The polymer is well known to be very stable against gamma or electron irradiation. This can be reasonably explained by H_2 evolution through interaction between excited benzence pendant molecules.

$$M^* + M \quad M + M + Hv$$
$$M^* + M^* \quad M\text{---}M + H_2, \qquad \text{in track.}$$

5.7 A Muon spin resonance experiment in hydrocarbons has shown that, at the end of the track of μ^+ in the medium, μ^+ spin interacts with surrounding radical species with a magnetic moment generated by himself (21). As a time dependent phenomenon, reactions of μ^+ and muomium with other species could be demonstrated.

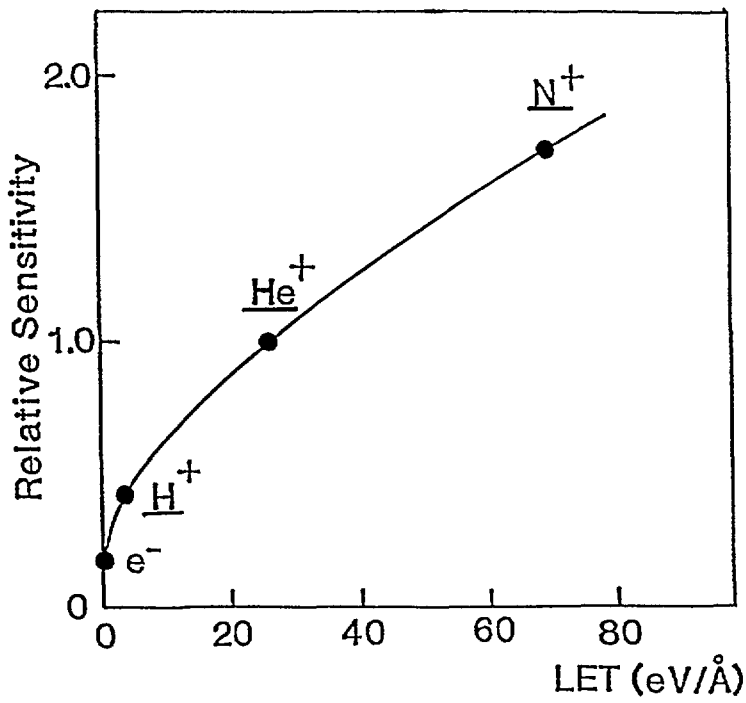

Fig. 6 Relative Sensitivity of Crosslinking in Polystyrene by Various Ion Beams (Normalized at 1MeV He^+ Ion)

6. Electronic and Nuclear Interaction of Charged Particles.

Radiation chemical effect mainly results from inelastic interaction (ionization and electronic excitation) with matter. It is known that nuclear recoil interaction can also contribute to chemical or biological effects.

Damage on biomolecules by protons depends very much upon the energy of the particle. One example is shown schematically in Fig. 7. There exists a minimum in the magnitude of the damage. At the lower energy side, the main effect comes from elastic recoil effect on atoms. On the other hand, at the higher energy side, the electronic excitation process becomes important.

Another example is concerned with radiolysis of solid KCN with various charged particles (22).

Depending on both kinds of charged particles and their energies, contribution to the radiolysis of KCN varies from eleastic (recoil) to inelastic (electronic), or vice-versa (22).

7. Conclusion

High LET radiation is characterized by:

Higher Level Excitation
Nuclear Recoil
High Density Excitation

Very specific physical and chemical effects could be expected, based upon their characteristic features of the high LET radiation.

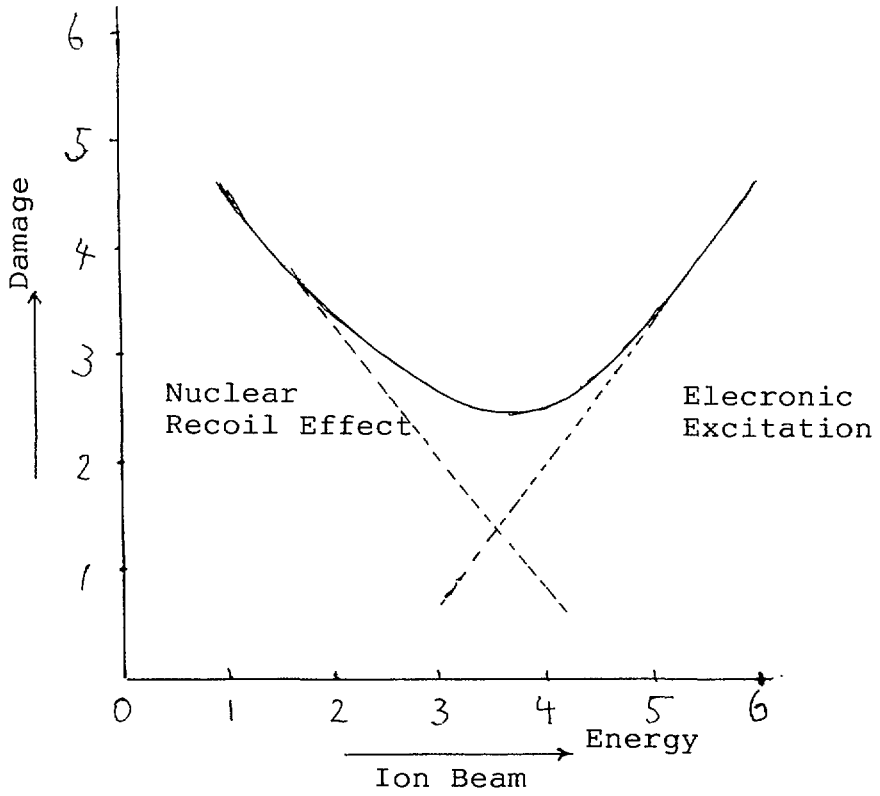

Fig. 7 Contributions of Nuclear Recoil and Electronic Effects on Damage of Some Biomolecules

Various examples mentioned above are demonstrating that very interesting specific phenomena, which can not be induced by either gamma or energetic electrons, can be seen.

All these phenomena occur within either spur or track:

$$M \longrightarrow (M^+(M^{+*}) + e^-)$$
$$\longrightarrow M^*, M^{**}$$
$$M^+ + e^- \longrightarrow M^*$$

The specific reactions are induced mainly by interaction among excited species:

1) $M^* + M$
2) $M^* + M^*$
3) $M^* + M^* + M^*$ } in track
4) nM^*

Process 1) is the main one for gamma or energetic electrons, For high LET radiation, 2) or 3) in the track become the essential processes.

$M^* + M^*$, $M^* + M^* + M^*$ do not exclude any kinds of combinations of excited states. It is expected that no reaction occurs for 1), but specific reactions can take place for 2), 3), and 4) under high density excitation.

The LET study and its application are fascinating fields of radiation research. Some interesting experimental results and facts have been clearly demonstrated. However, few explanations or elucidations have been made. Precise experiments and theoretical explanation will be needed for further development of the research.

Chemical reaction induced under high density excitation is a new field of chemistry. Therefore many phenomena and new applications could be expected in the near future in this field.

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BIOMEDICAL APPLICATIONS

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Abstract

Radiation processes for synthesis or modification of polymeric components of biomedical implants and devices are described in this chapter. These free radical processes include surface modification, polymerization and solid state treatments. Cobalt-60, electron accelerators and plasma gas discharge reactors are the most commonly used radiation sources.

1. Introduction

There is a wide variety of materials which are foreign to the body or other biological environments and which are used in contact with biologic fluids. These materials are called biomaterials. They include polymers, metals, ceramics, carbons, reconstituted or specially treated natural tissues, and composites made from various combinations of such materials. Some are needed only for short-term applications while others are, hopefully, useful for the lifetime of the individual. Applications include devices or implants for diagnosis or therapy, as well as a wide range of biotechnological uses (1).

Synthetic polymers make up the broadest and most diverse class of biomaterials. This is mainly because synthetic polymers are available in such a wide variety of compositions and properties and also because they may be fabricated readily into complex shapes and structures. Examples include fibers, rubbers, molded plastics, particulates, coatings, fluids, and porous solids. In addition, polymer surfaces may be readily modified physically, chemically, or biochemically. Such modifications can have significant influences on biologic responses to the biomaterials (2).

When a foreign material contacts blood or tissue fluids, the first measurable response in the initial seconds to minutes is the adsorption of large biomolecules - usually proteins (3,4). This is followed in the next minutes to hours by cellular interactions - especially platelets in blood and white blood cells or leukocytes in both blood and tissue fluids. Days later another important cell, the fibroblast, is involved in the healing process in tissue fluids. Important biologic responses in flowing blood include: activation of the complement and coagulation cascades leading to leukocytopenia and fibrin formation, respectively, platelet adhesion and aggregation, thrombus deposition, embolization and smooth muscle cell proliferation (near anastomoses of vascular graft implants). In the extravascular tissue space the inflammatory response to a foreign material also involves activation of the complement cascade plus a series of leukocyte stimulated "enzymatic attacks" at the material surface, often followed by collagenous fibrous tissue deposition by fibroblasts around (and sometimes within) the object (Table I).

Table I. Some Possible Biological Responses and Clinical Conditions Stimulated by Foreign Materials

Blood	Tissue Fluids
•Protein adsorption	•Protein adsorption
•Coagulation system activation and fibrin deposition	•Inflammatory response (acute and chronic)
•Complement system activation	•Complement system activation
•Leukocytopenia	•Fibrous tissue deposition, encapsulation
•Platelet adhesion, release, aggregation	•Biodegradation of polymer
•Thrombosis (platelet aggregation plus fibrin formation)	•Mineral (calcified tissue) deposition
•Embolization	•Infection
•Infection	•Tissue necrosis
•Mineral (calcified tissue) deposition	•Tumorigenesis (rare)
•Anastomatic hyperplasia and stenosis (in blood vessels)	

The important surface properties of biomaterials which can influence biologic responses are listed in Table II. It is probable that surface composition, mobility and topography all strongly influence the composition and organization of the initially adsorbed protein layer. It is this layer which mediates subsequent protein and cellular events at that interface. Figure 1 shows schematically the different changes in this protein layer which can occur after adsorption. The chemical and physical character of the biomaterial surface will strongly influence which one(s) of these changes will predominate with time (3). Furthermore, such changes will direct subsequent cellular interactions, which can determine the success or failure of an implant or device. Thus, a great deal of effort has gone into surface modifications of polymeric biomaterials.

2. Radiation Processes

There are three basic radiation processes which are utilized for preparing new or modified polymeric biomaterials. They are: 1) surface modification via (a) radiation graft copolymerization or (b) plasma gas discharge; 2) radiation polymerization of pure monomers(s) (a) in solution, (b) in an emulsion, or (c) in the solid state (e.g., below T_G); and 3) radiation crosslinking, in (a) a solution (b) the swollen state, or (c) the solid state. In addition, the modified polymers may be further modified by immobilization of biologically active molecules. Such biochemical processing can yield novel biomaterials having specific biological activity. Immobilization of biomolecules as enzymes, antibodies or drugs, and even cells, on or within the radiation-processed material can yield novel biofunctional biomaterial systems with great potential in medicine and biotechnology. Figure 2 summarizes radiation processing of biomaterials.

Table II. Surface Properties Influencing Biological Responses at Foreign Interfaces

1) Chemical composition (polar/apolar, acid-base, H-bonding, ionic charges)
2) Molecular motions (polymer chain ends, loops and their flexibility)
3) Topography (roughness, porosity, imperfections, gas microbubbles)
4) Domains (distributions of any of the above in the surface)

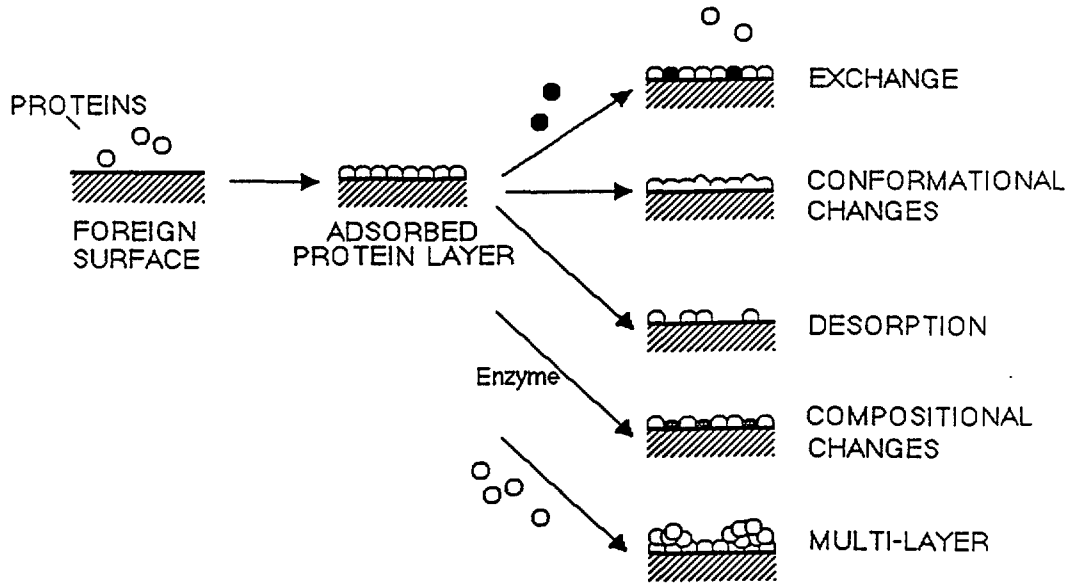

Fig.1. Possible modifications of the adsorbed protein layer with time after the initial layer is adsorbed

3. Surface Modification

Polymer surfaces may be modified physically, chemically, and/or biologically (Table III). Polymer surfaces are physically and chemically modified by physical deposition of other compounds or by direct chemical modification of the polymer surface. The most commonly used energy sources for surface modification are Cobalt-60 sources, electron beam ionizing radiations, and radio-frequency or microwave gas discharges, also called plasma or glow discharges (2,5,6). Photochemical reactions using U.V. light sources, and chemical agents as ozone may also be used, but they are less common. Figure 3 shows schematically the various chemical modification techniques and Table IV lists specific examples of physico-chemical modifications which have been used.

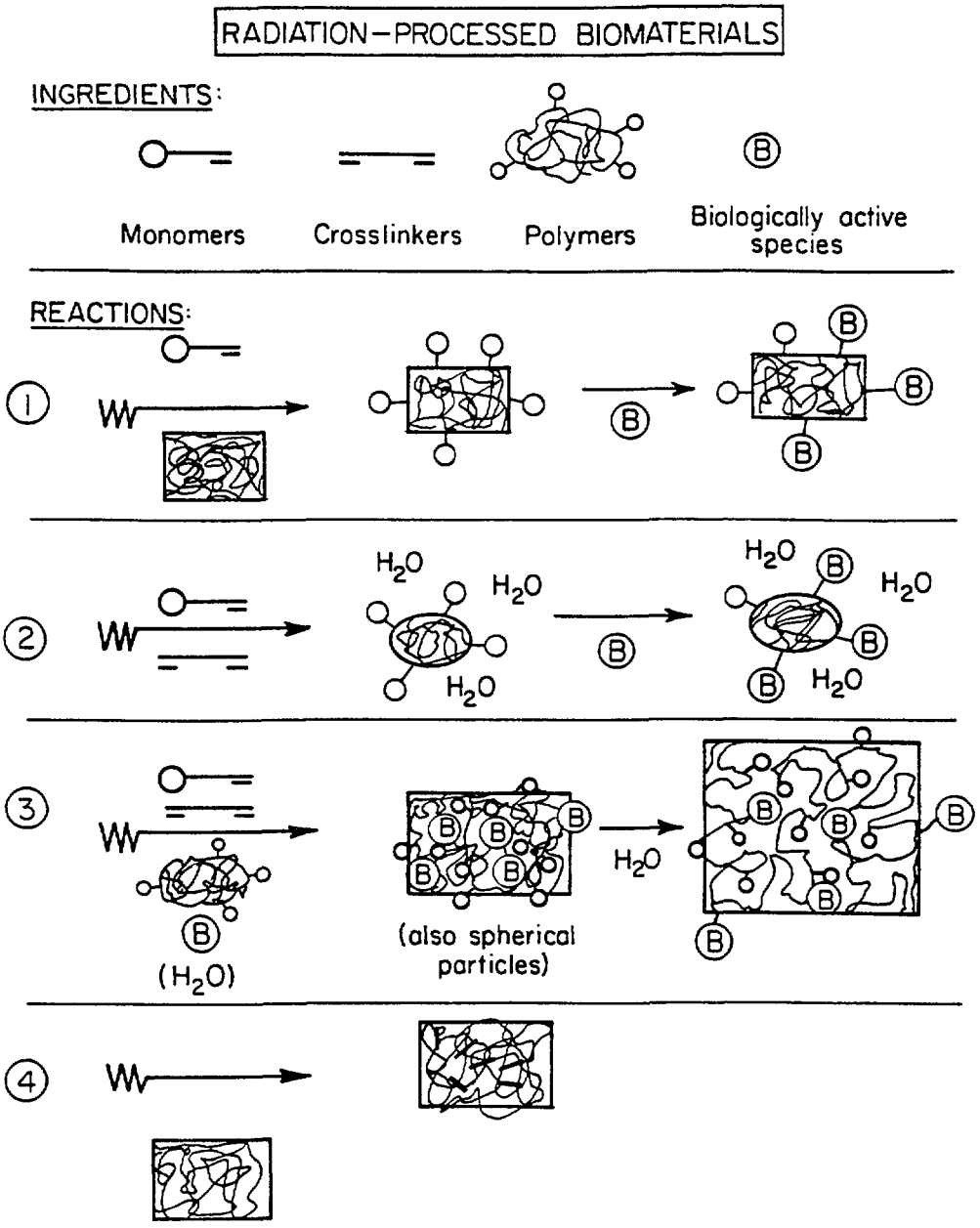

Fig.2. Radiation processes for producing new or modified polymeric biomaterials. Note that biomolecules (B) are chemically attached after processing or physically entrapped during processing (2)

3.1. Physico-Chemical Surface Modification

Hydrophilic polymer grafts on hydrophobic substrates have been especially studied and a number of reviews of these materials and their biological interactions have been published (2,5,6).

Ionizing radiation processing, in particular, offers unique advantages for preparing these novel biomaterials. Some of the obvious advantages are that

Table III. Biomaterial Surface Modification Techniques

I. *Physico - Chemical*

- **A) Physical deposition of coating**
- **B) Chemical modification**
- **C) Graft copolymerization**
  1. **Radiation**
  2. **Photochemical**
  3. **Ozone**
- **D) Plasma gas discharge**
  1. **Ablation (etching)**
  2. **Deposition**

II. Biological

- **A) Pre-adsorption of proteins**
- **B) Drug, enzyme immobilization**
- **C) Cell seeding**
- **D) Pre-clotting**

new polymers may be synthesized or existing polymers may be chemically modified by a relatively simple additive-free processing step at room temperature, sometimes with the potential for simultaneous sterilization. The doses used do not generally affect the polymer substrates properties significantly. Variation of the radiation dose and the grafting solution composition and temperature permits control of the extent and depth of grafting, graft-substrate interpenetration, and surface composition.

The plasma or glow discharge deposited coatings have different characteristics from radiation grafted surfaces (2,7,8). Their structure and composition depend importantly on the plasma conditions (e.g., gas pressure and flow rate, continuous or pulsed discharge, voltage and energy level). Their compositional make-up may be broad and contain a variety of chemical groups, as opposed to the rather well-defined radiation graft polymer. In addition, the coatings are usually tightly adherent , thin, and pinhole free. Porous systems are more difficult to treat uniformly through the pores. A recent article reviews biomedical applications of gas discharge processing (8).

3.2. Biological Surface Modification

Polymer surfaces may also be biologically modified, by pre-adsorption of a selected protein, immobilization of biomolecules such as antibodies, enzymes and drugs, seeding with cells, or pre-clotting with blood. Such biologic modifications may be carried out directly on the untreated polymer surface or following physico-chemical modifications of this surface, as described above.

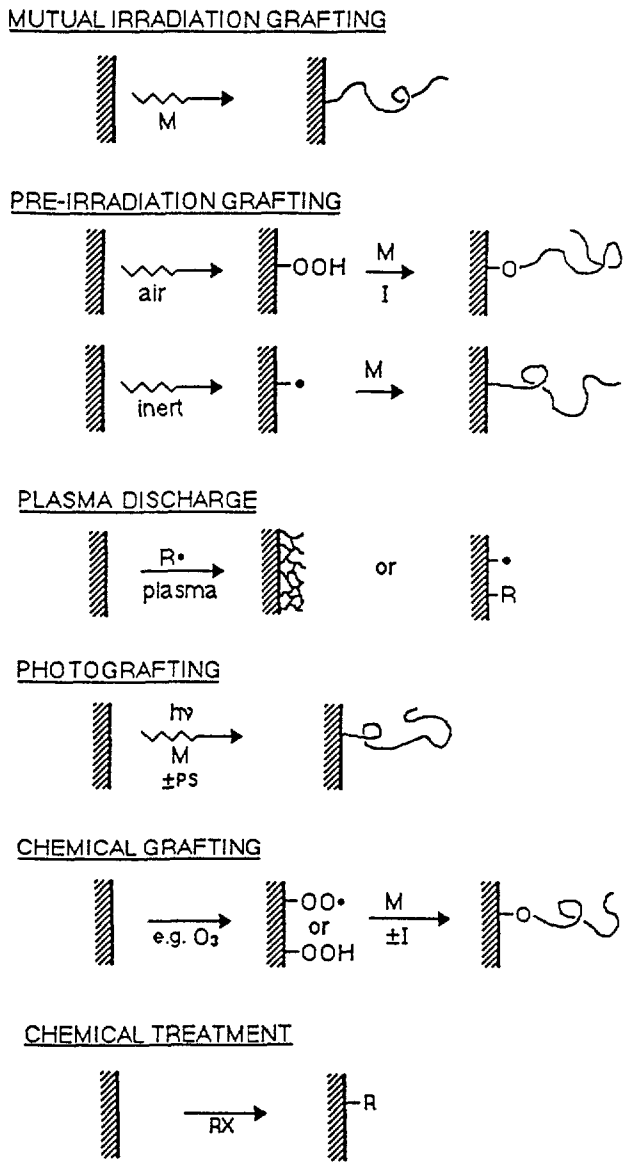

Fig.3. Methods for modifying the surface composition of polymers

Tables V, VI and VII present specific examples of biomolecules which may be immobilized and biological surface modification techniques and processes (9).

Chemical immobilization of a biomolecule involves specialized chemical reactions on specific backbone groups (usually $-NH_2$, -OH or $-CO_2H$) in order to activate these sites so they can form primary bonds with the species to be immobilized (often via $-NH_2$ groups on such species). This technique involves several steps. There has been extensive work using radiation processing plus chemical immobilization techniques (2,5,6). Radiation grafted hydrogels or radiation polymerized emulsions of HEMA or MAAc and their copolymers have been used for subsequent immobilization of biomolecules. Rembaum and co-workers pioneered in this area, immobilizing antibodies on radiation-polymerized polymeric emulsions (10,11). Hoffman and co-workers also pioneered in the immobilization of biomolecules as heparin and streptokinase on radiation grafted hydrogels (12). Extension of these studies has led to

Table IV. Examples of Physico-Chemical Surface Modifications

A) Physical deposition of coatings
- •polyurethanes
- •FFSR (filler free silicone rubber)
- •cationic soaps (for heparin binding)
- •polyethylene oxides (for non-fouling surface)

B) Chemical modification
- •heparin-like groups
- •lipophilic groups (to attract albumin)
- •polyethylene oxides (for non-fouling surface)
- •-OH blocking esters (to avoid complement activation)

C) Graft Copolymerization
- •hydrogels
- •hydrophilic/hydrophobic copolymers
- •lipophilic groups
- •heparin-like groups

D) Plasma gas discharge
- •silanes
- •fluorocarbons
- •hydrocarbons
- •acidic, basic or polar compounds (to deposit reactive groups as -COOH, $-NH_2$, or -OH)

interesting and novel surface grafts containing immobilized biomolecules (13). Fig. 4 illustrates one newer approach for graft copolymerization of a monomer-conjugated enzyme (13,14).

Plasma treatments are also useful for surface immobilization of biomolecules. This technique can be less controlled as well as less efficient than surface immobilization or radiation grafted polymers due to the large number of poorly characterized chemical groups produced on a plasma treated surface. Gombotz, et.al. used gas discharge deposited allylamine polymers to subsequently immobilize a non-fouling polyethylene-oxide coating (15). Kiaei, et.al. have shown that fluorinated gas discharge coatings strongly retain physically adsorbed proteins (16). This has been utilized by Safranj, et.al. for an immunoassay having enhanced sensitivity (17).

Table V. Examples of Biological Surface Modifications

A) Presorption of proteins
- albumin (passivating)
- fibronectin (promotes cell adhesion, growth)

B) Drug, enzyme, and antibody immobilization
- heparin (anti-thrombogenic)
- prostaglandins (anti-platelet release, aggregation)
- enzymes (fibrinolysis, bioreactors, disease treatment)
- antibodies (immunoassays, targeted drug delivery, affinity separations)

C) Cell seeding
Endothelial cells (for vascular grafts)

D) Pre-clotting
Fresh whole blood (for vascular grafts)

Table VI. Biologically Active Species which may be Immobilized within or on Radiation-Processed Polymeric Biomaterials

Enzymes
Antibodies
Antigens
Anti-thrombogenic agents
Antibiotics
Antibacterial agents
Contraceptives
Anticancer Agents
Drug antagonists
Other drugs, in general
Sugars and polysaccharides
Cells

Table VII. Some Sequential Surface Modification Processes for Polymeric Biomaterials

1) Deposit a cationic soap or radiation graft a polycation	→	ionically bind heparin
2) Radiation graft a hydrogel or chemically modify surface or treat in polar gas discharge	→	chemically immobilize biomolecule
3) Deposit lipophilic groups (chemically or via radiation grafting)	→	hydrophobically bind albumin
4) Adsorb fibronectin	→	seed with endothelial cells
5) Treat in a gas discharge	→	adsorb fibronectin

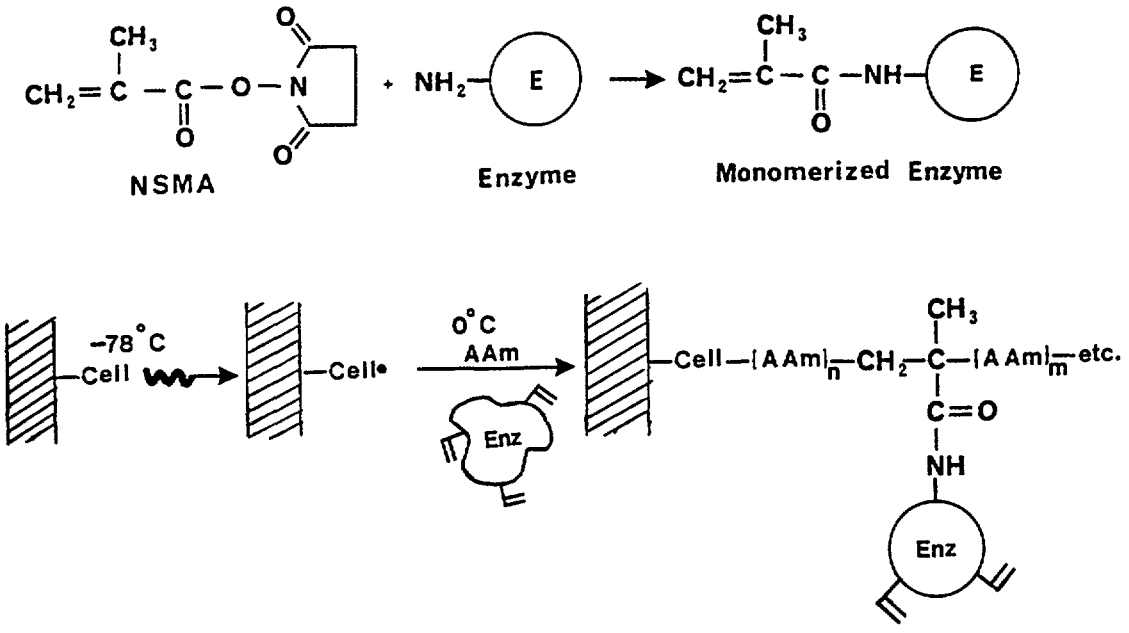

Fig.4. New radiation graft method for immobilizing a monomer-conjugated biomolecule as an enzyme (13)

4. Polymerization

Kaetsu and coworkers have immobilized a number of enzymes and drugs by low temperature radiation polymerization of glassy hydrophilic monomer solutions containing the biomolecules, dissolved or suspended within them (18,19). The hydrogel polymerizations actually occur during the warming step, as the frozen-in radicals become mobile above the glass temperature. This low temperature process is mild and does relatively little damage to the biomolecule compared to that which would occur during a room temperature radiation polymerization. Albin, et.al. have applied this low temperature process for synthesis of an immobilized glucose oxidase glucose sensor - insulin delivery system. (20).

5. Bulk Property Modification

The only significant biomedical application of ionizing radiation processing for bulk polymer modification is sterilization. There have been a few references to radiation crosslinking of polyethylene in orthopedic prostheses, but this technique has not been of great interest to fabricators of such implants, despite the attractiveness of such a clean process which has the capability of simultaneous sterilization.

6. Conclusions

Radiation processing with Cobalt-60 sources, electron accelerators and plasma gas discharge reactors are all being extensively pursued for improvement of exciting biomaterials, as well as for synthesis of new and exciting biomaterials. These "clean" and facile techniques offer great promise for the next century.

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GRAFTING AND CURING ON POLYMER SURFACES — ROLE OF ADDITIVES

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Abstract

The role of novel additives in accelerating grafting processes initiated by both ionising radiation and UV is discussed. The additives reported are mineral acids, specific organic compounds like urea, inorganic salts and polyfunctional monomers, particularly acrylates. A unique mechanism for the function of these additives is proposed. The concept of additive effects has been extended to fast polymerisation reactions, especially curing processes initiated by electron beams and high pressure UV lamps. Common additives are found to accelerate both grafting and curing processes. The value of this result for observing concurrent graft with cure is discussed. The mechanistic contribution of ions to the currently accepted free radical process for both grafting and curing initiated by ionising radiation is considered from basic studies with Fourier Transform ion cyclotron resonance mass spectrometry.

1 INTRODUCTION

Radiation grafting and curing processes are useful polymerisation techniques for modifying surfaces to give products with unique properties [1,2]. One of the critical parameters in this work is the total radiation dose required to achieve minimum grafting and curing levels. Much current research is directed towards the discovery of additives which will sensitise both grafting and curing processes. The use of a number of such additives in both grafting and curing is discussed in this paper. The model system chosen for grafting is the copolymerisation of styrene to the polyolefins and cellulose initiated by both ionising radiation and UV. The two radiation grafting techniques essentially act in a complementary manner, UV requiring simpler equipment but the use of photoinitiators to achieve practical grafting levels within reasonable irradiation times. Additives reported here include mineral acids, specific organic compounds like urea, inorganic salts and multifunctional acrylates (MFAs). Mechanistic studies of these additive effects in grafting have been performed using a novel technique involving tritium labeled styrene.

Extension of this grafting work to UV and EB rapid curing systems is also discussed. Concurrent grafting with curing can be an advantage in improving the properties of the finished product. Mechanistically both radiation grafting and curing reactions are considered to be free radical processes, however, recent relevant work [3] using a novel mass spectrometric technique, involving, Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICRMS) indicates that ionic intermediates may also play a role in these present radiation polymerisation systems. Details of the FTICRMS studies will be reported.

2 EXPERIMENTAL

2.1 Grafting procedures

The following modification of grafting methods previously reported were used in these experiments [1,2]. Low density polyethylene film (0.12mm), isotactic polypropylene film (0.06mm) were cut into pieces approximately 40x30mm. Cellulose samples were cut from Whatman No.41 ashless filter paper and equilibrated for at least 24 hours at 20°C and 65% relative humidity before and after use. For the actual grafting experiments, polyolefin or cellulose

samples were immersed in the prepared grafting solutions in 150x25mm stoppered tubes and irradiated for the requisite period of time in a 1200 Ci cobalt 60 source. After irradiation the samples were removed from the solution and washed with methanol to remove acid. Polyethylene and polypropylene samples were then extracted for 72 hours at 25°C in a soxhlet apparatus with benzene, whilst the cellulose sample were washed with chloroform to remove homopolymer. Films were air dried and then dried at 40°C to constant weight. Final weight was determined after 24 hours at 20°C and 65% relative humidity. Percentage graft was calculated by the increase in weight divided by the original weight.

2.2 Distribution studies

For this work, tritium labeled styrene was made by the reaction of styrene and tritium gas over a palladium barium sulphate catalyst [4] and diluted immediately to an activity of approximately 1mCi/ml by styrene which had not been freed of inhibitor. For the actual distribution studies, polyethylene substrates were immersed in methanolic solutions of tritiated styrene maintained at 25°C in a water bath. After a given time the film was blotted dry and immediately transferred to an extraction solution of 1,4-dioxane for one week. The styrene content was determined by liquid scintillation counting expressed as mg of styrene absorbed per g of film. The detection limit was 1mg/g with a reproducibility of ±1%. Alternatively the styrene content was determined by gas chromatography, the detection limits being 4mg/g ±5% for styrene. Tritiated styrene solutions in 1,4-dioxane were counted on a low background, double headed, coincident liquid scintillation counter using Bray's solution as liquid scintillator [5].

2.3 Molecular weight determination

Polymer samples were dissolved in tetrahydrofuran (0.25% w/v) and clarified by passing through a swinney filter of pore size 0.45 μm. Approximately 10μl was injected into a Waters Associates model ALC-GPC 201 high pressure liquid chromatograph with two columns - μ Bondagel E - high A ($1.5x10^4$ - $7x10^6$) and μ Bondagel E - linear ($2x10^3$ - $2x10^6$), operating with a flow rate of 1ml/min, a backpressure of 1100 - 1400 psi and an attenuation factor of 8. Detection was by refractive index and ultra violet detectors and data reduction was performed on a Waters Associates model 730 data module with GPC options. Monodispersed polystyrene standards were used for calibration and all results are expressed in terms of number average molecular weight relative to these linear polystyrenes.

For the analysis of the polymer in the grafted cellulose the copolymer was hydrolysed in the following manner. Grafted cellulose was allowed to swell for 24 hours in a mixture of acetone, dimethylformamide and water (15:4:1). An equal portion of aqueous sulphuric acid (75% v/v) was added. The mixture was allowed to stand for 2 hours, diluted with water to be 6% in H_2SO_4 and refluxed for 24 hours. The digest was extracted with toluene and the polymer precipitated by dropwise addition of methanol.

2.4 UV and EB curing

Two systems were used for both UV and EB rapid cure experiments. The UV lines were (i) a Primarc Minicure unit with lamps of 200 watts per inch, and (ii) a Fusion system of 300 watts per inch. The EB facilities were a 500 kV Nissin machine and a 175 kV ESI unit. For the actual application of the materials, appropriate resin mixtues containing the oligomers, monomers, additives and sensitisers (UV) were coated onto the substrate, the material placed on a conveyer belt and then exposed to the radiation sources.

2.5 Mass spectrometry work

Spectra were run on a Bruker Spectrospin CMS47 FTICRMS and a VG MM16F single focus magnetic instrument. Ionisation was accomplished with 70eV electrons for positive ion spectra and 5eV for negative ion spectra. The VG MM16F was operated at 70eV 50μ amp trap current for EI and 150eV, 1 amp emission current for CI with an accelerating voltage of 4000V. Pressures used were 10^{-7} - $5x10^{-9}$ millibar in the FTICR and 10^{-5} for EI, and $5x10^{-1}$ for CI in the VG instrument.

3 RESULTS AND DISCUSSION

3.1 Additives for enhancing grafting

A range of additives have been discovered for enhancing grafting reactions initiated by UV and ionising radiation [1,6]. Typical results for grafting involving representative additives are shown in Table 1. Thus in the grafting of styrene dissolved in methanol to polyethylene using gamma rays the inclusion of a mineral acid such as sulphuric (0.2 M) increases the grafting yield at all monomer concentrations studied up to 50%. Even at this concentration, which corresponds to the Trommsdorff peak, significant enhancement in yield is observed. Similar results are obtained when UV replaces gamma rays as initiator for the same grafting system, benzoin ethyl ether (BEE) being the UV sensitiser for the process.

TABLE 1 Synergistic effect of acid and TMPTA as additives for enhancing UV and ionising radiation grafting of styrene in methanol to polyethylene film

Styrene (% v/v)	Graft (%)							
	Gamma Ray [a]				UV [b]			
	N.A.	H+	T	T + H+	N.A	H+	T	T + H+
20	14	19	-	-	28	14	28	41
30	37	51	39	54	101	126	52	78
40	76	81	73	106	189	193	321	266
50	109	134	137	181	124	107	412	525
60	89	73	105	101	37	31	133	188

[a] Dose rate of 4.1×10^4 rad/h to 2.4×10^5 rad with sulfuric acid (2.0×10^{-1} M) and trimethylolpropane triacrylate (T) at 1% (v/v) with low density polyethylene film (0.12 mm); N.A. = no additive.

[b] Irradiated at 24 cm for 24 h from 90 W medium pressure UV lamp. Other conditions as in footnote a. Benzoin ethyl ether (1% w/v).

When polyfunctional monomers (PFMs) are used as additives to replace acid in the same gamma ray and UV grafting systems, increases in grafting yields are also observed at certain monomer concentrations (Table 1). For this purpose the most commonly used PFMs are MFAs such as trimethylolpropane triacrylate (TMPTA). In the UV system, the enhancement with TMPTA is particularly large especially at the Trommsdorff peak. This suggests that the acrylate groups in TMPTA may also be sensitising the grafting reaction to complement the BEE.

The grafting enhancement profiles of both acid and MFA are different. Thus synergistic effects of the two additives are found in grafting with both gamma rays and UV. Again the synergistic effect with UV is more pronounced than with ionising radiation, especially at the Trommsdorff peak.

The replacement of acid with inorganic salts, typified by lithium nitrate, leads to increases in grafting yields again with both gamma ray and UV as initiators in the model system reported in Table 2 for the grafting of styrene in methanol to polypropylene. With lithium nitrate as additive the grafting enhancement in both radiation systems predominates at lower monomer concentrations. Addition of TMPTA to the styrene solution containing lithium nitrate results in a synergistic effect of the two additives in grafting similar to that found previously with mineral acid and TMPTA. This effect is particularly obvious at the lower monomer concentrations typically 30% for both radiation systems.

TABLE 2 Synergistic effect of lithium salts with TMPTA as additives for enhancing UV and ionising radiation grafting of styrene in methanol to polypropylene

Styrene (% v/v)	Graft (%)							
	Gamma Ray [a]			UV [b]				
	N.A.	Li^+	$T+Li^+$	B	Li^+	$B+Li^+$	B+T	$B+T+Li^+$
20	14	30	29	5	2	10	100	126
30	64	52	123	24	1	38	297	529
40	72	35	83	45	2	20	496	337
50	44	23	49	31	2	14	283	221
60	32	-	15	22	5	13	281	-
70	26	-	-	15	4	11	-	-

[a] N.A. = no additive; $Li^+ = LiNO_3$ (0.2 M); T = TMPTA (1% v/v); irradiated at 7.5×10^4 rad/h to 2.5×10^5 rad.

[b] B = benzoin ethyl ether (1% w/v); irradiated at 24 cm from 90 W lamp at 20°C, other conditions as in footnote a.

3.2 Mechanism of additive effects

The mechanism for grafting enhancement due to acid and salt effects appears to be different to that attributed to the presence of MFAs. Considerable work has been undertaken with the mechanism of acid and salt additives, particularly with the former, in an attempt to optimise the affect for practical purposes.

3.2.1 Acids and salts. Acid enhancement in grafting was originally discovered in gamma ray initiated systems [1,7]. The mechanisms proposed for the effect at that time involved essentially two factors, (i) the radiolytic yield of hydrogen atoms G(H) and (ii) the extent to which grafting polymer (polystyrene) was solubilised in the bulk solution. Solvent structure was also considered to be important, those solvents with high radiolytic yields of hydrogen atoms such as methanol and the lower molecular weight alcohols, being efficient reagents for grafting. These observations were explained in terms of the abstraction of hydrogen atoms from the trunk polymer PH by those H atoms to yield additional grafting sites as shown in equations 1 to 3.

$$CH_3OH + H^+ \longrightarrow CH_3OH_2^+ \quad (1)$$

$$CH_3OH_2^+ + e \longrightarrow CH_3OH + H\cdot \quad (2)$$

$$PH + H\cdot \longrightarrow P\cdot + H_2 \quad (3)$$

The above mechanism has since been shown to be an over simplification of the grafting process since it fails to explain a number of subsequent observations reported [1,7,8] including (i) the occurrence of enhancement only at certain acid and monomer concentrations, (ii) the efficacy of sulphuric, perchloric and nitric over other acids, (iii) the presence of grafting enhancement in the pre-irradiation and post irradiation techniques where radiolytically produced hydrogen atoms are not available and (iv) acid enhancement in photosensitised grafting where radiation chemistry effects are not relevant.

More recent mechanistic studies [9] of acid and salt enhancement effects have been performed by measuring the uptake of styrene monomer by polyethylene in the presence of additive. The technique involves the use of tritium labelled styrene. This is a convenient and sensitive improvement over related methods for the investigation of grafting behaviour. The approach

minimises the need for extrapolation inherent in the swelling experiments of other authors [7]. The directness of the method also means that it is likely to be less susceptible to interference than the method of styrene extraction reported previously [10]. Above all, the technique has the advantage of measuring the actual uptake and, at short times, is free of errors introduced by possible thermal polymerisation within the film.

The results (Table 3) show conclusively, that, at certain monomer concentrations and under the radiation grafting conditions used, the presence of additives in the graft solution leads to a higher degree of styrene absorption by the backbone polymer with the potential for more styrene molecules to participate in grafting resulting in an increase in yield.

TABLE 3 Variation in styrene absorption from methanol solution by polyethylene with time[a] using labelled monomer technique

Time of Swelling (h)	Styrene Absorption (mg styrene / g polyethylene)	
	No Additive	H_2SO_4 (0.1M)
0	0	0
0.5	38.8	42.8
1.0	40.5	44.3
2.0	42.5	45.8
12.0	45.6	53.3
20.0	45.4	54.0

[a] Technique used involved tritiated styrene with 30% styrene in methanol solutions (% v/v) and polyethylene film (0.12 mm) at 25°C. The styrene was tritiated by palladium catalysed exchange with T_2O. Scintillation counting was used to determine tritium.

Additional information from acid and salt enhancement in grafting involving monomer concentrations close to the Trommsdorff peak is also mechanistically relevant. Thus the data in Table 4 show the magnitude of this enhancement using the grafting of styrene in methanol to cellulose system. In this example lithium perchlorate is used as the salt, appearing to be more effective than lithium nitrate reported in earlier tables. These results with cellulose are important because with this backbone polymer the grafted material can be digested, graft copolymer separated and the molecular weight of the material can be determined. The values in Table 5 for $\bar{M}_n$ the number average molecular weight of the grafted copolymer, for the samples in Table 4, indicate a relationship between the enhancement in grafting yield and corresponding molecular weight of the grafted polymer.

The results from all the experiments reported in Tables 3, 4 and 5 indicate that the mechanism for the acid and salt effects can be explained in terms of increased partitioning of nonpolar monomer into the grafting region of a nonpolar substrate and of the polymer which has already been grafted at the substrate surface. Methanol is too polar to swell polyethylene except in very small amounts so most of the swelling is due to styrene entering the substrate. The reverse applies to cellulose which is well swollen by methanol. The increased partitioning proposed is similar to the well known salting out effect. The greater polarity of methanol solution containing dissolved electrolyte results in more of the nonpolar styrene being distributed preferentially into the substrate. The increased rates of monomer entry and the increased equilibrium concentrations in the substrate are high enough to achieve the increased yields which are found when the substrate is immersed in the solution. The higher concentration of monomer at the grafting site favours propagation of growing chains. The enhanced grafting yield is usually associated with a

TABLE 4 Effects of acid and lithium perchlorate in radiation grafting[a] of styrene in methanol to cellulose[b] under conditions close to Trommsdorff peak

Styrene (%)	Graft % No Additive	H_2SO_4 (0.1M)	$LiClO_4$ (0.2M)
15	32	34	54
20	66	120	155
25	106	153	159
30	112	95	96
35	110	60	80

[a] Irradiation in air at 24°C, dose rate 3.3×10^4 rad/h, total dose 5.0×10^5 rad.
[b] Whatman 41 filter paper.

TABLE 5 Comparison of acid with lithium perchlorate on number-average molecular weights ($\bar{M}_n$) of copolymer from radiation grafting[a] of styrene in methanol to cellulose[b] under conditions in table 4

Styrene (%)	$\bar{M}_n$ ($\times 10^5$) No Additive	H_2SO_4 (0.1M)	$LiClO_4$ (0.2M)
15	3.5	4.8	3.7
20	5.0	9.8	8.0
25	7.7	10.0	10.0
30	12.0	8.6	9.0
35	9.2	7.6	7.0

[a] Irradiation in air at 24°C, dose rate 3.3×10^4 rad/h, total dose 5.0×10^5 rad.
[b] Whatman 41 filter paper.

corresponding increase in molecular weight and there is no evidence for any increase in the number of chains initiated. There does not appear to be any necessity to invoke radiolytic effects such as greater hydrogen atom yields due to the presence of the additive to explain the enhancement effect as a predominant process. Polar monomers are not readily salted out by electrolytes in methanol solution and therefore the degree to which they would exhibit acid and salt effects in a grafting system would be lower than that expected for nonpolar monomers.

3.2.2 Polyfunctional monomers PFMs such as TMPTA appear to enhance grafting in a different manner to that of acids and salts with both UV and ionising radiation. PFMs appear to have a dual function, namely to enhance the copolymerisation and also crosslink the grafted polystyrene chains (Figure 1). In the grafting experiments branching of the growing grafted polystyrene chains occurs when one end of the polyfunctional monomer, e.g. TMPTA, immobilised during grafting is bonded to the growing chain. The other two ends are unsaturated and free to initiate new chain growth by scavenging reactions. These branched polystyrene chains may eventually terminate cross-linked by reacting with another polystyrene chain or an immobilised TMPTA radical. Grafting is thus enhanced mainly through branching of the grafted

polystyrene chains. A comparison of the UV and ionising radiation data indicates that the magnitude of the increase in grafting yield is much higher in the photochemical system particularly with the MFAs, thus suggesting that in the UV the acrylate groups in the TMPTA act as additional sensitisers to complement the BEE for the grafting process.

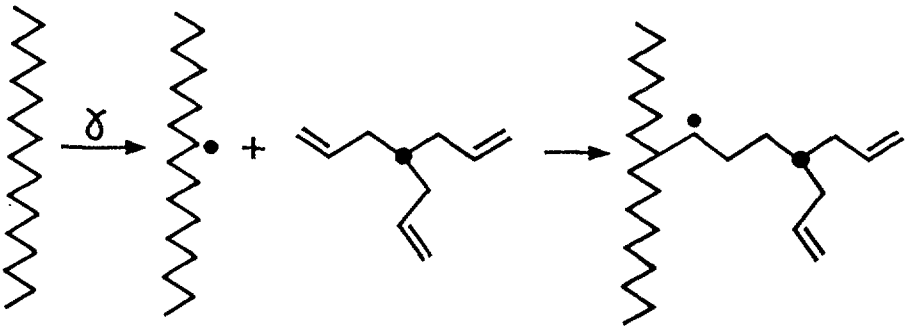

FIGURE 1 Reaction mechanism of multifunctional acrylate with polymer radical by gamma radiation

3.3 Preparative importance of additive effects in grafting

The present additive effects are important in a preparative context since radiation graft copolymers are now being used in many applications and any technique for reducing the radiation dose to achieve a particular percentage graft is of both practical and economic significance. The discovery of a range of salts to complement acid, already known, as additives for enhancing grafting is useful, since the scope of the enhancement technique is very much expanded. Thus grafting systems which may have been sensitive to acid can now be treated with metal salts to achieve the same type of enhancement. By contrast, if solubility problems in the grafting solution occur with the latter additive, acid can be used as an alternative.

The observation that PFMs, in particular MFAs, exhibit strong synergistic effects with these additives is also of significant preparative importance in grafting. In this respect not only do the MFAs exhibit synergistic effects with the previous two classes of additives in grafting yield they also exhibit synergistic effects in grafting efficiency with these same additives (Table 6). The data show that acid and PFMs using divinylbenzene (DVB) as an example, not only increase grafting yields, they also enhance the competing homopolymerisation, however the former reaction is preferentially affected to the benefit of the overall process. Thus the monomer is used efficiently in the grafting process in the presence of the additives. These developments involving grafting enhancement will be particularly beneficial for those processes involved in modifying surfaces of relatively inert materials where generally high radiation doses (5 megarad) are required to achieve even low copolymerisation yields [11]. Under these relatively high radiation doses not only can the structure of the backbone polymer be detrimentally affected but also internal crosslinking of the grafted copolymer can occur to yield a surface which is unsuitable for many applications. By the use of current synergistic affects the radiation dose required to achieve a particular level of radiation graft can be significantly reduced, to limits where no adverse radiolytic affects in the finished copolymers are observed.

3.4 Additive effects in curing reactions

Additive affects are also important in radiation processing particularly radiation rapid cure reactions where films of oligomer/monomer are polymerised in a fraction of a second using UV lamps and low energy electron beam (EB) machines. An important property of these systems is adhesion to the substrate since the process essentially involves curing a film of polymer onto the substrate, bonding being predominantly through physical forces. With certain substrates, e.g. organics, the possibility of concurrent grafting occurring with cure is relevant since adhesion and flexibility in the final product can be improved. In curing formulations, additives are used to

TABLE 6 Synergistic effect of acid and DVB on the grafting efficiency of styrene in methanol to polyethylene film initiated by ionising radiation[a]

Styrene (% v/v)	Grafting Efficiency[b] (%) N.A.	H^+	H^+ + DVB
30	56.2	59.4	58.8
40	73.9	83.0	74.2
50	75.1	79.4	85.2
70	45.7	41.2	65.4

[a] Dose rate of 1.0x104 rad/h to 2.4x10^5 rad; N.A. = no additive; H+ = H2SO4 (0.2M); DVB (1% v/v); low density polyethylene film (0.12mm).
[b] Ratio (graft/graft + homopolymer) x 100.

control slip, gloss,flow, viscosity etc. These are typified by the fluorinated ester, urea and the silane used in Table 7. In order to examine the potential affect of these additives on concurrent grafting during curing, the additives have been examined for their effect in a conventional UV grafting process. The results in Table 7 indicate that for the photografting of styrene to polypropylene, both urea and the fluorinated ester enhance graft whereas the silane is a retarder, presumably due to the repulsion affect of the silicon atom. However the significant feature of these results is evident when TMPTA is added to the grafting solution containing these commercial additives. The presence of TMPTA markedly enhances the graft (Table 8) despite the presence of the silane retarder. The mechanistic role of MFAs in curing formulations would thus appear to be more subtle that hitherto considered. The MFA not only speeds up cure and crosslinking it can also markedly affect the occurrence of concurrent grafting during cure. In this respect the effect of structure of MFA on grafting is interesting. The data in Table 9 show that TMPTA > PETA > DPGDA. The monofunctional methacrylate HEMA is the least reactive of all. Thus the structure of the MFA is very important in affecting the degree to which grafting can occur in UV and EB radiation grafting processing.

3.5 Mechanism of grafting and curing - role of ions

Currently it is acknowledged that the mechanism of the grafting and curing processes initiated by ionising radiation and discussed in this paper are predominatly free radical reactions. The possibility that ions may participate in these processes has recently received preliminary attention

TABLE 7 Effect of organic additives (urea, silanes, fluorinated alkylesters) on photografting of styrene to polypropylene[a]

Styrene in methanol (% v/v)	Graft (%) N.S.	BEE	BEE + U	BEE + U + Si	BEE + U + FE
20	< 5	< 5	< 5	< 5	< 5
30	< 5	35	30	18	23
40	< 5	39	46	31	53
50	< 5	17	19	13	16
70	< 5	14	11	7	10

[a] Irradiated 8h at 24cm from 90W lamp at 20°C ; N.S. = no sensitiser ; BEE = benzoin ethyl ether (1% w/v)-sensitiser ; U = urea (1% w/v) ; Si = silane (1% v/v) : Z-6020 supplied by Dow ; FE = fluorinated alkyl ester (1% v/v) : FC-430 supplied by 3M.

TABLE 8 Effect of TMPTA in presence of organic additives in photografting of styrene to polypropylene[a]

Styrene in methanol (% v/v)	Graft (%) N.S.	BEE	BEE + U	BEE + additives + TMPTA
20	< 5	< 5	< 5	260
30	< 5	35	30	588
40	< 5	39	46	711
50	< 5	17	19	368
70	< 5	14	11	131

[a] Conditions as in Table 7 ; additives used were urea, silane and fluorinated alkyl ester ; TMPTA (1% v/v).

TABLE 9 Effect of structure of multifunctional acrylate as additive in photografting of styrene to polypropylene[a]

Styrene in methanol (% v/v)	Graft (%) N.A.	TMPTA	PETA	DPGDA	HEMA
20	< 5	38	24	29	< 5
30	35	190	188	186	61
40	39	603	426	356	44
50	17	366	133	178	36
70	14	179	78	89	26

[a] Conditions as in Table 7 ; BEE (1% w/v) as sensitiser in all runs; N.A. = no additive; acrylate monomers (1% v/v); TMPTA = trimethylolpropane triacrylate; PETA = pentaerythritol tetracrylate ; DPGDA = dipropylene glycol diacrylate ; HEMA = hydroxyethyl methacrylate.

[3] from basic studies involving mass spectrometry where the primary effects of electron bombardment on monomers has been investigated, particularly in relation to ion formation. Early work [12] from mass spectrometry indicated that ionic intermediates may be involved in the liquid phase polymerisation of isobutylene with radiation initiation, however no analogous studies were reported with acrylates. Acrylate monomers, particularly MFAs are important constituents in EB curable mixtures, thus detailed electron impact studies from these monomers could be valuable in the present context. The recent development of Fourier Transform Ion Cyclotron Resonance mass spectrometry (FTICRMS) has created a powerful tool for such studies. As a guide to the information provided by the two types of mass spectrometric studies used in this paper, mass spectrometric data for a typical MFA, namely TMPTA, are shown in Table 10. Fragmentation under electron impact conditions is significantly greater in the magnetic sector instrument (VG) reflecting the effect of enhanced temperature in the VG inlet (50° to 100°C) on the resulting spectrum compared with the room temperature operation of the FTICR. Evidence for ion molecule reactions in the mass spectrometer is shown by the peak at m/z 297 in the chemical ionisation mode of the FTICRMS.

Additional mass spectrometry data relevant to the present discussion are provided in Figure 2. These are preliminary FTICRMS data from one of the most valuable monomers used in EB curing, namely TPGDA. The data demonstrate the effect of time on the TPGDA spectra. Thus under chemical ionisation conditions in the FTICR instrument with TPGDA, the ion of m/z 113

TABLE 10 Spectra of TMPTA under various mass spectrometric conditions[a]

MS	m/z	RI	m/z	RI	m/z	RI	m/z	RI	m/z	RI	m/z	RI
EIVG	296	6	225	1	224	1.5	169	3	152	15	140	6
	127	7	124	5	69	6	68	12	56	8	55	100
	43	25	41	12	39	5	29	10				
EIFT	296	2	225	60	169	6	152	40	140	12	139	10
	137	8	127	14	124	10	123	8	97	8	69	10
	55	10										
CIFT	297	10	225	100								

[a] Spectra run on Bruker Spectrospin CMS47 FTICRMS (FT) and a VG MM16F single focus magnetic instrument (VG); CI = chemical ionisation; EI = electron impact; m/z = mass/charge of ion; RI = relative intensity (%); molecular ion at m/z = 296; CIFT at 2 seconds.

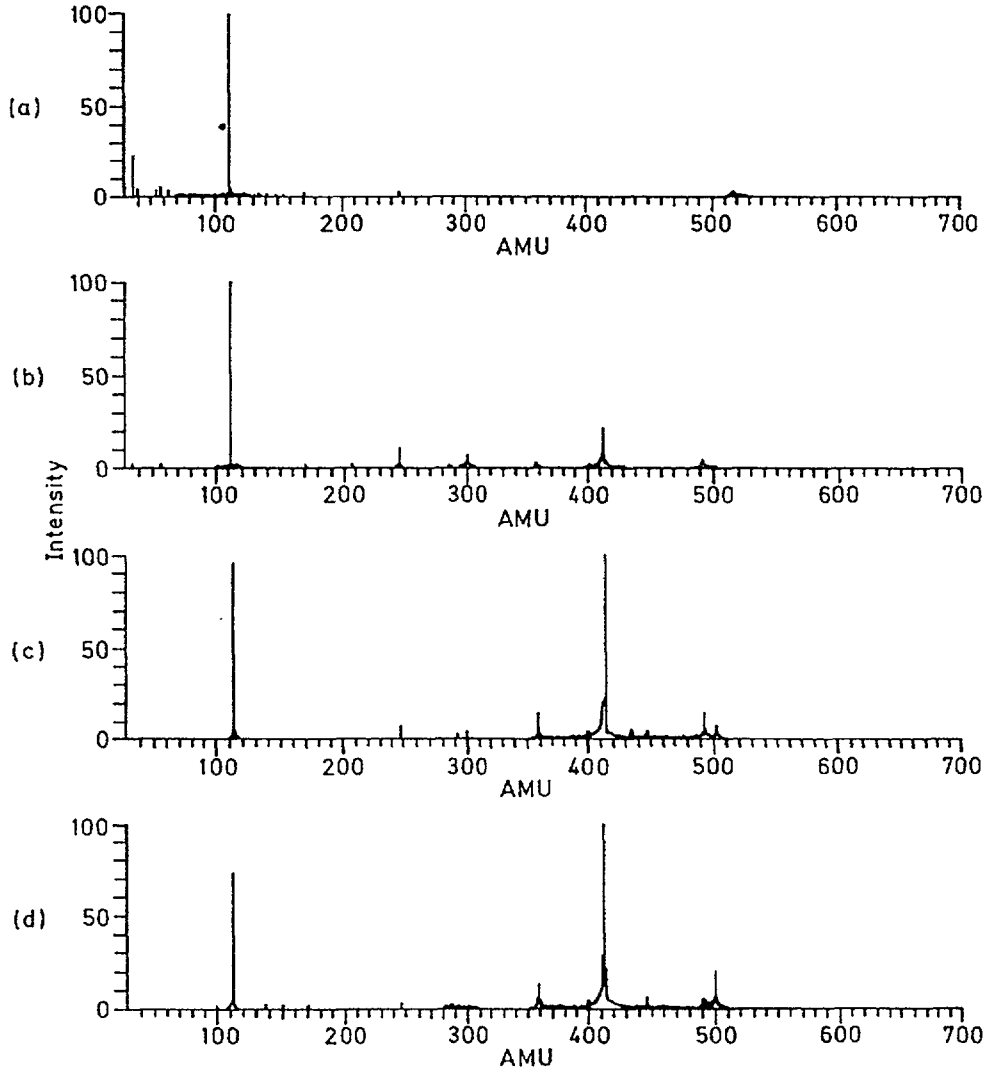

FIGURE 2 FTICR spectra for TPGDA (molecular ion m/z 300) (a) EI, (b) CI 2sec, (c) CI 20sec, (d) CI 60sec.

remains large in all spectra. However as the time allowed for ion interactions is increased other ions at higher m/z increase progressively in intensity such that after 60 seconds m/z 113 is no longer the largest ion but is replaced by ions at 512, 403 and 359, presumably formed by ion molecule reactions involving fragments of the sample molecules. There thus appears to be an increase in molecular weight species, i.e. oligomerisation with time.

These data offer an interesting mechanistic interpretation of EB curing reactions. The fact that ions with m/z higher than the molecular ion are formed from fragments and molecules in the FTICR as the time of rotation increases, indicates that ion molecule reactions involving cationic species as depicted in equation 4 are favoured processes in this system.

$$R^+ + M \longrightarrow RM^+ \quad \text{(where R = fragment, M = TPGDA)} \qquad (4)$$

Thus a plausible explanation for the formation of the ion at m/z 413 is an ion molecule process where R is the fragment $-CH_2(CH_3)CHOCOCH{=}CH_2$ from M which is TPGDA. Importantly these species constitute the predominant ions in the FTICR spectrum over the time scale used. As the trend in (b) to (d) Figure 2 shows, over longer time scales even higher molecular weight species, i.e oligomerisation reactions occur. Assisting this process would be the degree of fragmentation experienced by the monomer in the beam since the radiation stability of the monomer is important in this interpretation. The comparison of the electron impact mass spectrum of TPGDA at room temperature and 50°C indicates that fragmentation occurs at the higher temperature. The implication of these observations in EB processing relate to the temperature at which the monomer/oligomer coating is applied and cured. Certain EB lines coat at 50°C, thus the types of polymers formed under the beam from the same monomer/oligomer formulation may yield different structures and hence different properties depending on the temperature at which the line operates.

The other important feature of these data are that the same types of reactions are observed in the negative ion mode of the FTICR as are observed above with positive ions. These are gas phase observations but they raise the interesting possibility that analogous ionic processes can occur in condensed phases, such as curing and grafting reactions, especially utilising electrons from EB machines delivering very high dose rates. Under these conditions, compared with the gas phase, the frequency of collisions in condensed phases would be very much lower, however, the efficiency of such collisions in condensed phases would be higher due to cage effects and mobility considerations. If conditions can be found where ionic processes predominate in these fast polymerisation processes for the same radiation dose, then products possessing new properties may be capable of being made. Previously ionic processes in radiation polymerisation systems were only considered to occur under extremely anhydrous conditions, however this conclusion may need to be modified due to these recent mass spectrometric studies.

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POLYMER RADIATION CHEMISTRY

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Abstract

This article reviews some of the work carried out in the Polymer and Radiation Group at the University of Queensland over the past ten years. The objective of the work has been to investigate the relationships between polymer structure and sensitivity towards high energy radiation, including ^{60}Co gamma radiation, electron beams and UV radiation. A range of synthetic polymers containing carboxyl groups, acrylate groups, sulfone groups, amide linkages and aromatic residues have been investigated.

1. Introduction

There has been increasing interest recently in studies of the effects of ionizing radiations on polymers. The use of polymeric materials in the electronics and related industries, the energy industry, and the increasing industrial use of radiation processing has been responsible for this trend.

Investigations of the physical and chemical changes which take place in polymers when they are exposed to ionizing radiation have generally relied upon studies of the radiation chemistry of simple small molecule model compounds. These studies have played an important role in the research of radiation sensitive polymers of the type described here. In order to identify the important steps in the degradation reactions a variety of chemical techniques have been employed, including: ESR spectroscopy to identify radical intermediates and to determine their yield; NMR spectroscopy to examine changes in tacticity and chemical composition; gas chromatography to identify volatile molecular products and to measure their yield; and gel permeation chromatography, osmometry, viscosity and ultra centrifugation to determine changes in molecular weight and molecular weight distribution.

2. Radiation Effects

The primary event which occurs when ionizing radiation interacts with a molecule involves the ejection of an electron to form a cation radical, as shown in equation 1.

$$A \xrightarrow{\sim\sim} A^{+\cdot} + e^{-} \qquad [1]$$

The ejected electron may become trapped on a site in the matrix of the material to form an anion radical, equation 2.

$$B + e^{-} \longrightarrow B^{-\cdot} \qquad [2]$$

Alternatively, the electron may be captured by a cation radical to produce an excited state molecule as shown in equation [3]

$$A^{+\cdot} + e^{-} \longrightarrow A^{*} \qquad [3]$$

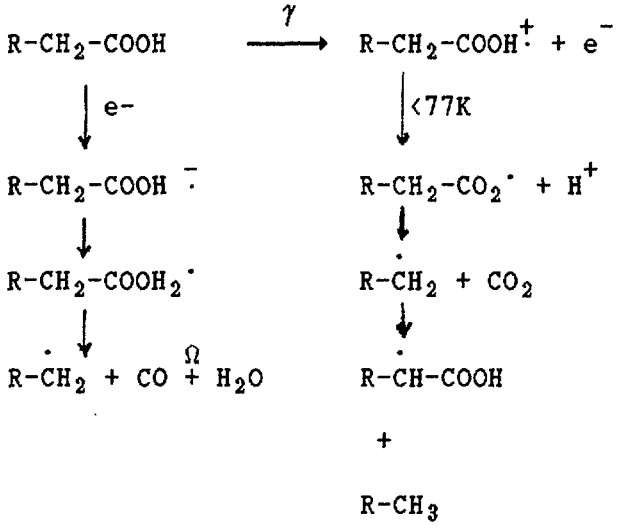
The cation radicals, anion radicals and excited states species are reactive and generally undergo further chemistry, even at low temperatures. For example, the radical cation can decompose into a neutral radical and a cation, which is often H^{+}. The anion radical can react with cations, for example, remove H^{+}, to form neutral radicals. Excited states species may decompose via a variety of processes including (a) homolytic scission to form two neutral radicals (b) heterolytic scission to form a cation and an anion, or (c) bond rupture to form two neutral molecules. If neutral radicals are formed, these too may undergo further reaction. In polymers these reactions may result in crosslink formation, depropagation reactions, changed stereochemistry of the polymer, or the formation of grafts, as well as a variety of other processes.

The reactions of anion and cation radicals, excited states and neutral radicals have been studied by the University of Queensland Polymer and Radiation Chemistry Group, for a variety of radiation sensitive polymers and model compounds. The polymer systems considered include:

1. Poly(carboxylic acid)s
2. Poly(acrylate)s
3. Aromatic polymers and copolymers
4. Copolymers of styrene
5. Poly(amino acid)s
6. Poly(sulfone)s
7. Polyolefins

2.1 Polycarboxylic Acids

The radiation chemistry of small carboxylic acid molecules have been widely investigated [1]. The major processes which have been identified are summarized below:



The radicals showed at 77K are anion radicals and decarboxylation radicals [1]. In some compounds secondary, hydrogen abstraction radicals may also be observed. The preferred site for hydrogen abstraction is alpha to the carboxyl group. If the temperature is increased above 77K, the anion radicals become unstable, and they decompose to form decarboxylation, and

ultimately hydrogen abstraction radicals. The hydrogen abstraction radicals remain stable until the melting point is approached.

This mechanism is also supported by the observed molecular products which include carbon dioxide, carbon monoxide and the parent hydrocarbon, together with smaller amounts of alkene, hydrogen and other hydrocarbons [1].

The yields of radical intermediates and decarboxylation products (CO + CO_2) are approximately equal as shown in Table I.

Table I

G(R·) observed at 77K and G(CO + CO_2) observed at 298K for model carboxylic acids

Acid	G(R·)	G(CO+CO_2)
CH_3COOH	4.9	4.4
CH_3CH_2COOH	6.7	4.9
$CH_3(CH_2)_2COOH$	5.4	5.0
$(CH_3)_2CHCOOH$	5.7	5.9
$(CH_3)_3CCOOH$	5.2	6.3[(a)]

(a) observed at 80°C

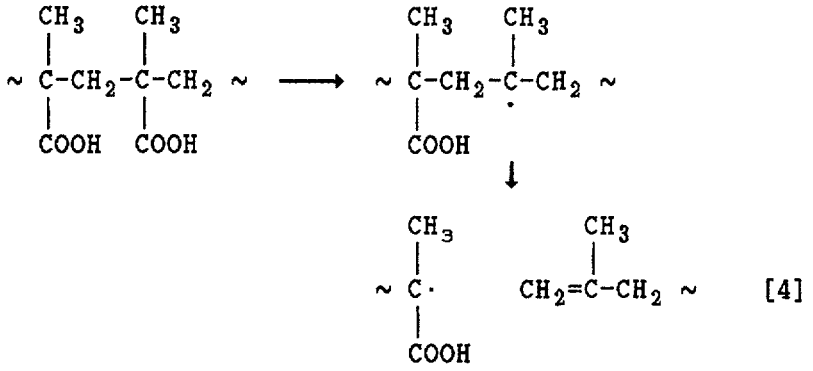
The gamma radiolysis of homopolymers of acrylic, itaconic and methacrylic acids can be explained on the basis of the small molecule studies. They also undergo decarboxylation reactions, but the yields of (CO + CO_2) are much greater for the polyacids than for the corresponding small molecule models [1]. However, the yields of radical intermediates are similar to those observed for the model compounds. These yields are compared in Table II. The higher yields of carbon monoxide and dioxide have been interpreted as being indicative of some decomposition via excited states species [1].

Table II

G(R·) and G(CO + CO_2) for radiolysis of polyacids at 303K

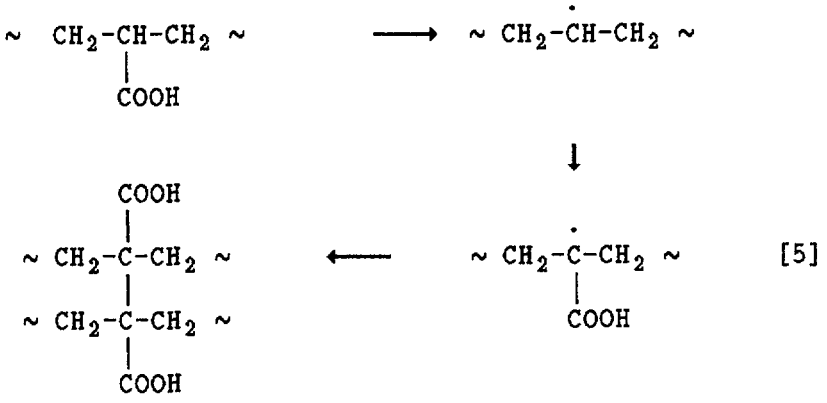
Polyacid	G(R·)	G(CO+CO_2)
Acrylic	3.8	12.1
Methacrylic	3.1	10.7
Itaconic	3.1	5.4

While the observed stable radical intermediate for polyacrylic acid was the α-carbon radical, as expected on the basis of the model compound studies, that observed for polymethacrylic acid was the propagation radical. This observation can be explained if the polymethacrylic acid decarboxylation radical is unstable and undergoes β scission, as shown below in equation 4:



[4]

Molecular weight studies [2] have confirmed that polymethacrylic acid only undergoes scission on gamma radiolysis with G(S) = 6.0, while polyacrylic acid undergoes only crosslinkig with G(X) = 0.44, as shown in equation 5:



[5]

2.2 Polyacrylates

Polymethacrylate and polymethyl methacrylate both undergo side chain scission yielding primary radicals similar to those found in the corresponding polyacid. The major radical species present at room temperature following radiolysis of polymethyl acrylate is the hydrogen abstraction radical I formed with G(R·) = 0.88 [3].

I II

The primary radical formed by side chain scission in polymethyl methacrylate undergoes β scission, as does polymethacrylic acid, to produce the propagating radical II observed at room temperature. The G value for production of this radical at 298K has been reported to be equal to 2.1 [4].

The volatile products formed on radiolysis of both polymethyl acrylate [5] and polymethyl methacrylate [6] are mainly H_2, CO, CH_4 and CO_2. The yields of these gases are given in Table III. These products result from fragmentation of the ester group after side-chain scission.

Molecular weight studies following gamma radiolysis of PMA and PMMA confirm that PMA undergoes mainly crosslinking (G(S) = 0.17 and G(X) = 0.48 at 298 K [7]) while PMMA undergoes scission G(S) = 1.7 [4].

Table III

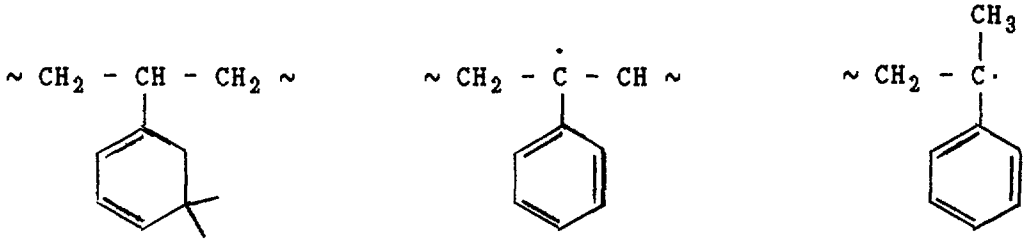
G-values for the major volatile products of radiolysis of polymethyl acrylate and polymethyl methacrylate at 303K.

Product	PMA	PMMA
H_2	0.43	0.34
CO	0.28	1.08
CH_4	0.50	0.66
CO_2	0.21	0.68

2.3 Polystyrenes

The radiation chemistry of polystyrene and poly-α-methyl styrene provide interesting comparisons with those of the corresponding poly(acrylate)s discussed previously.

Radiolysis of polystyrene and poly-α-methyl styrene at 77 K both result in the formation of anion radicals and cyclohexadienyl radicals III, with total radical yields of approximately 0.4 [8] and 0.1 [8] respectively, as the major radical components. At room temperature, the major radical component formed on radiolysis of styrene is the cyclohexadienyl radical, with a smaller yield of α-carbon radicals IV. The total radical yield is 0.12 at 298 K [4].



III IV V

Radiolysis of poly-α-methyl styrene at room temperature results in formation of cyclo-hexadienyl radicals and propagation radicals V. The total radical yield at this temperature is 0.05 [8].

Thus, the major difference between the styrenic polymers and the acrylic polymers is the capability of the styrenic polymers to scavenge hydrogen atoms to form cyclohexadienyl radicals, which are stable at room temperature. This process protects the polymer from further degradation.

The radical yields for the aromatic polymers are much smaller than for the acrylic polymers, which has been explained in terms of the capability of the aromatic ring to degrade excitation energy, which might otherwise result in bond scission.

Molecular weight studies following radiolysis of these polymers show that polystyrene undergoes nett crosslinking leading to gel formation (G(S) = 0.009 and G(X) = 0.043) [9]. On the other hand, poly-α-methyl styrene has been found to undergo scission only with G(S) = 0.3 [8]. Thus, in this respect, polystyrene and poly-α-methyl styrene behave in a manner similar to that for the corresponding poly(acrylate)s.

2.4 Copolymers of Styrene and Acrylics

The yields of radical intermediates and volatile molecular products resulting from radiolysis of polystyrene are much smaller than those found for radiolysis of the poly acrylate. This has been explained by the protective nature of the aromatic side chain. It is of interest to consider the range of this protective effect through studies of random copolymers of styrene and methyl methacrylate or methyl acrylate.

The variation in the radical yields for the range of copolymers of styrene and methyl methacrylate is shown in Figure 1 for radiolysis at 298 K [4]. A protective effect of the aromatic residues is clearly present and is

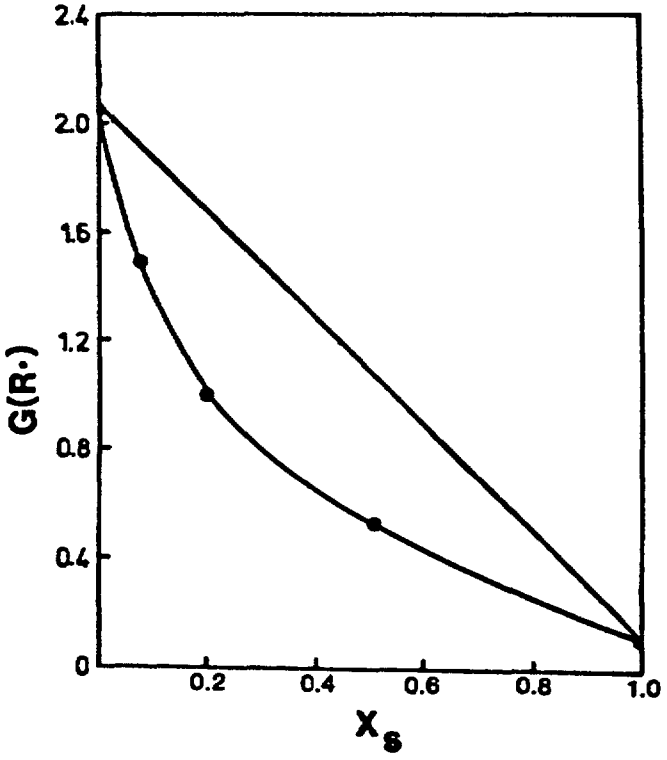


Figure 1: The radical yield G(R·) versus mole fraction styrene in the polymer X_S for radiolysis of styrene-methylmethacrylate copolymers at 303 K.

a maximum for polymers containing 30 percent styrene. This composition corresponds to a point at which the average sequence length of the methyl methacrylate units is two. That is, on average, each methyl methacrylate has at least one styrene neighbour.

A corresponding protective effect has been found for the yields of gaseous molecular products as shown in Figure 2 [6].

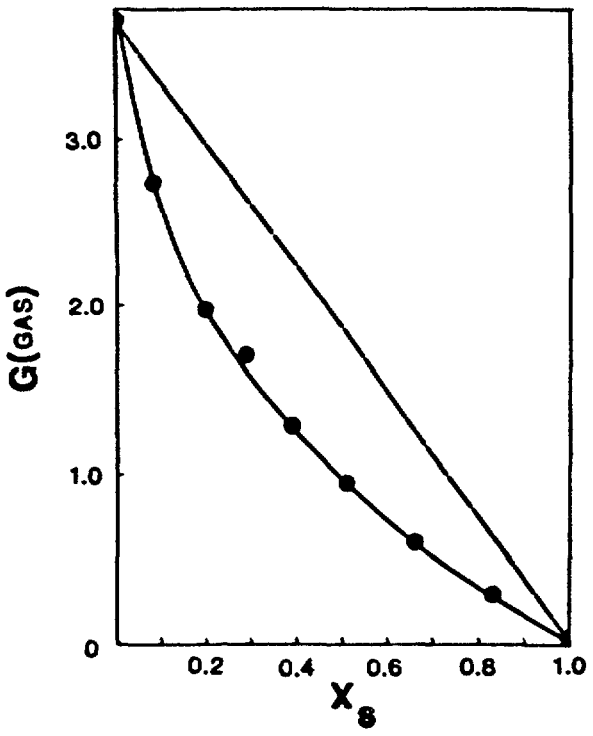


Figure 2: The total gas yield G(gas) versus the mole fraction of styrene in the polymer X_S for radiolysis of styrene-methylmethacrylate copolymers at 303 K.

Similar studies on copolymers of methyl acrylate and styrene, as well as a range of other comonomers, for example acrylonitrile, methacrylic acid and ethylene, have demonstrated that the protective mechanism occurs in these copolymers and that the range of influence of the styrene residues is comparable with that found for copolymers of methyl methacrylate.

2.5 Polyamino Acids

Polyamino acids contain an amide linkage in the backbone polymer chain. This linkage is similar to that found in synthetic polyamides such as nylon. Radiolysis of polyamino acids with aliphatic side chains results in (i) scission of the main chain and (ii) scission of the side chain [10].

The major radical intermediates observed at room temperature are α-carbon radicals VI formed by hydrogen abstraction by primary radicals or, if the side chain in the amino acid is branched, as in valine, side chain radicals VII, but these are formed in lower yield.

VI VII

The major volatile products formed on radiolysis of these polymers result from cleavage of the side chain to form the corresponding alkane, and elimination of a fragment of the main chain to form acetamide. Some ammonia and carbon monoxide are also produced.

A comparison of the yields of alkane products, resulting from side chain scission and fragmentation; of nitrogen containing products resulting from elimination of acetamide or ammonia; and of radical intermediates, is given in Table IV.

Table IV

G-values for formation of alkanes, nitrogen products and radical intermediates following radiolysis at 298K.

Polyaminoacid	G(alkane)	G(N)	G(R·)
Glycine	-	3.3	2.2
Alanine	2.7	3.8	2.9
Valine	5.0	4.1	3.0

The approximate correlation between the values for the various product yields given in Table IV suggests that the chemical processes responsible for side chain scission, elimination of main chain segments, and formation of polymer radicals are closely related [10]. This proposal is supported by the observation that aliphatic polyaminoacids undergo nett scission on gamma radiolysis [10], and that the scission yield has been estimated to be in the range 2-7 [11].

The radiation chemistry of the poly(amino acid)s with aromatic side chains, for example polyphenylalanine and polytyrosine, is similar to that for the aliphatic amino acids, but the radiation chemical yields are smaller due to the protective effect of the aromatic groups [10]. Copolymers of amino acids which contain aromatic residues together with residues containing a radiation sensitive group, for example poly(glutamic acid-co-tyrosine), demonstrate that the protection of the aromatic group is greatest for next neighbour residues [12], as was observed for copolymers of styrene.

2.6 Polysulfones

Poly(olefin sulfone)s have the general structure:

$$\sim CH_2 - \underset{\displaystyle R}{\underset{|}{CH}} - SO_2 \sim$$

These polymers are particularly sensitive to ionizing radiation and undergo main-chain scission with a G(S) $\simeq$ 10. This large value is due to selective scission of C-S bonds. Sulfur dioxide and olefin are the major radiolysis products. The yields of these products increase rapidly with temperature near the ceiling temperature. A simple depolymerization of the polymer would lead to equal yields of olefin and sulfur dioxide according to equation 6:

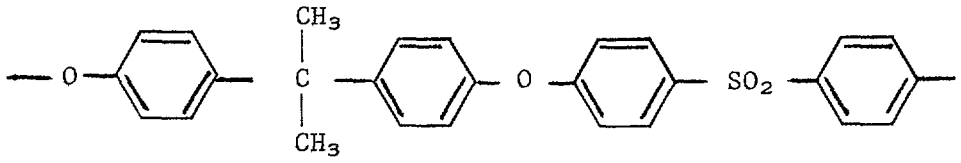
$$\sim CH_2 - CHR - SO_2 \sim \overset{K}{\rightleftharpoons} CH_2 = CHR + SO_2 \qquad [6]$$

However, the ratio of $G(SO_2)/G(olefin)$ is considerably greater than one [13]. In addition, there may be a substantial amount of isomers of the olefin monomer produced.

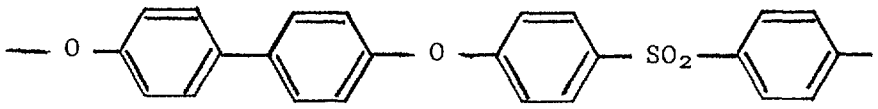
These results have been explained [14] in terms of a mechanism in which, following formation of the polymer cation radical, the C-S bond breaks forming a cation and a radical, with the cation located on the sulfur group and the radical on the carbon. After primary scission, the following processes can take place: (i) depropagation by both radical and cation; (ii) cationic homopolymerization of free, product olefin, initiated by a polymer carbonium ion; (iii) isomerization in the formation of olefin via a carbonium ion intermediate. The relative importance of these reactions is determined by the lifetime of the carbonium ion.

The proposed mechanism has been supported by studies on small molecule model compounds of dialkyl, alkyl-aryl and diaryl sulfones [15].

By contrast with the poly(alkene sulfone)s, the aromatic poly sulfones have been found to exhibit resistance to damage by ionizing radiation. For example, Brown and O'Donnell [16] found $G(SO_2)$ = 0.02 and G(total gas) = 0.04 for Bis-A polysylfone at 303 K.



Bis-A polysulfone



Biphenyl polysulfone

A recent study [17] of the radiation chemistry of a series of aromatic sulfone homopolymers and copolymers has shown that biphenyl groups are more effective protecting groups than bisphenol-A or hydroquinone groups. For example, at 423 K $G(SO_2)$ is 0.15 for bisphenol-A-polysulfone; 0.14 for hydroquinone polysulfone and 0.06 for biphenyl polysulfone. For copolymers of these compounds, the G-value is linearly dependent on composition. The enhanced protection by the biphenyl group is also reflected in the crosslinking and scission yields; for bisphenol-A polysulfone G(S) = 0.68 and G(X) = 0.64 and for biphenyl polysulfone G(S) = 0.48 and G(X) = 0.40. In these polymers crosslinking is believed to occur via the endlinking mechanism [18].

Acknowledgements

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