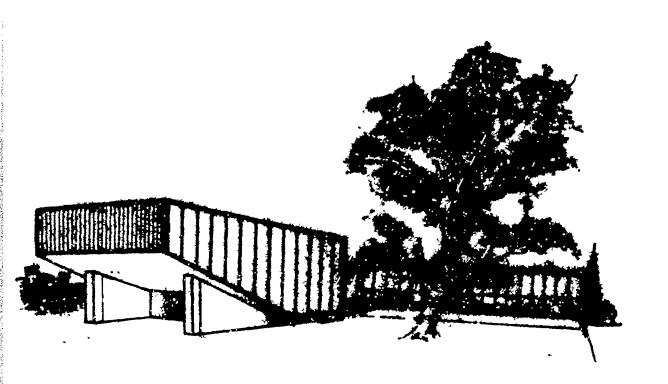
AUSTRALIAN INSTITUTE OF NUCLEAR SCIENCE AND ENGINEERING

15th AINSE RADIATION CHEMISTRY CONFERENCE 5-7 NOVEMBER, 1990

LUCAS HEIGHTS - AINSE THEATRE

In association with the Polymer Division RACI



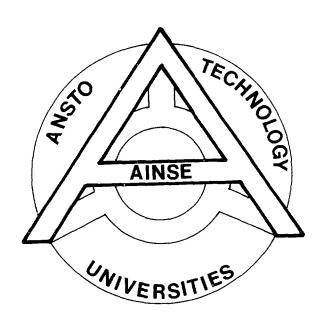
CONFERENCE HANDBOOK

(Programme, Abstracts and General Information)

AUSTRALIAN INSTITUTE OF NUCLEAR SCIENCE AND ENGINEERING 15TH AINSE RADIATION CHEMISTRY CONFERENCE 1990

LUCAS HEIGHTS N.S.W.

In Association with the Polymer Division Royal Australian Chemical Institute



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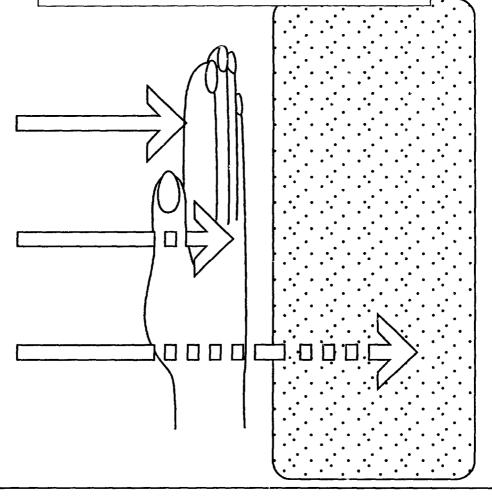
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SUMMARY

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<u>Session III</u> 3.40 - 5.00	Technology) <u>Ions and Free Radicals in Gases</u> <u>Chairman</u> : Mr D.F. Sangster (ANSTO)
Session IV 5.00 - 6.00 6.45 - 7.00	Poster Session Conference Dinner Sutherland Trade Union Club 77 Manchester Road, GYMEA Conference Address (Professor F.P. Larkins (Uni. of Tas & Melb)
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Session VI 11.00 - 12.40	Radiation Degradation of Polymers II Chairman: Dr J. Guthrie (Uni. of Leeds)
<u>Session VII</u> 1.40 - 3.30	Radiation Polymerisation Processes Chairman: Dr R. Clough (Sandia Nat. Labs, New Mexico)
<u>Session VIII</u> 3.50 - 5.50	Effects of Radiation on Polymers Chairman: Prof D.H. Napper (Uni. of Syd)
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Session XI 11.20 - 12.20 12.20 - 12-30 2.00 - 3.30	Radiation Effects Chairman: Dr G.S. Laurence (Uni. of Adel) Closing Remarks: Dr T.I. Quickenden Conference President Laboratory Visits - ANSTO Depart ANSTO Reception

Monday 5th November, 1990 - Lucas Heights

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12.00 - 12.40	3R <u>Review</u>	Radiation Chemistry and Radiotherapy. R.F. Martin (Peter MacCallum Cancer Inst.)
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2.40 - 3.00	6	Radiolytic and Photolytic Studies of Luminescent Defects in Irradiated Solids. K. Caulfield, R. Cooper, D. Edmondson (Univ. of Melbourne), J. Boas (Aust. Rad. Lab.)
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Monday 5th November, 1990 - Lucas Heights

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4.40 - 5.00	10	Electron-Ion Recombination in Noble Gases. R. Bhave, R. Cooper, R. Van Sonsbeek, K. Caulfied (Univ. of Melbourne)
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	12	Photodegradation of PVC Systems. D.J.T. Hill, <u>F. Kroesen</u> , J.H. O'Donnell, P.J. Pomery (Univ. of Queensland)
	13	Electron Energy Loss in Irradiated Molecular Gases. R. Bhave, R. Cooper (Univ. of Melbourne)
	14	A Search for Electrochemically Induced Cold Nuclear Fusion. T.I. Quickenden, R.W. Brunning, T.A. Green (Univ. of W.A.)
	15	$O_2(A^3\Sigma_{\bullet}^+ \rightarrow X^3\Sigma_{\bullet}^-)$ Herzberg I Emission from UV Irradiated H ₂ O and D ₂ O Ices. A.J. Matich, T.I. Quickenden (Univ. of W.A.), M.G. Bakker (Argonne Nat.Lab.), C.G. Freeman (Univ. of Canterbury, N.Z.)
	16	The Use of Novel Additives in Radiation Grafting. P. Dworjanyn (Univ. of N.S.W.)
	17	Electron Spectroscopic Studies of the Adsorption of Carbon Tetrachloride on Oxidised Ni(110). M.A. Chester (Univ. of East Anglia, U.K.), R.B. Fahim (Univ. of El-Minia, Egypt), D. Lennon (Univ. of W.A.)

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	19	Polymerisation of Microemulsions using Gamma-Radiolysis. R.A. Mann, R.G. Gilbert, D.H. Napper (Univ. of Sydney)
	20	Some Additions to the Pulse Radiolysis Facility. M.L. Turonek, <u>G.S. Laurence</u> (Univ. of Adelaide)
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		CONFERENCE ADDRESS Professor F.P. Larkins (Univs. of Tasmania & Melbourne)

Tuesday 6th November, 1990 - Lucas Heights

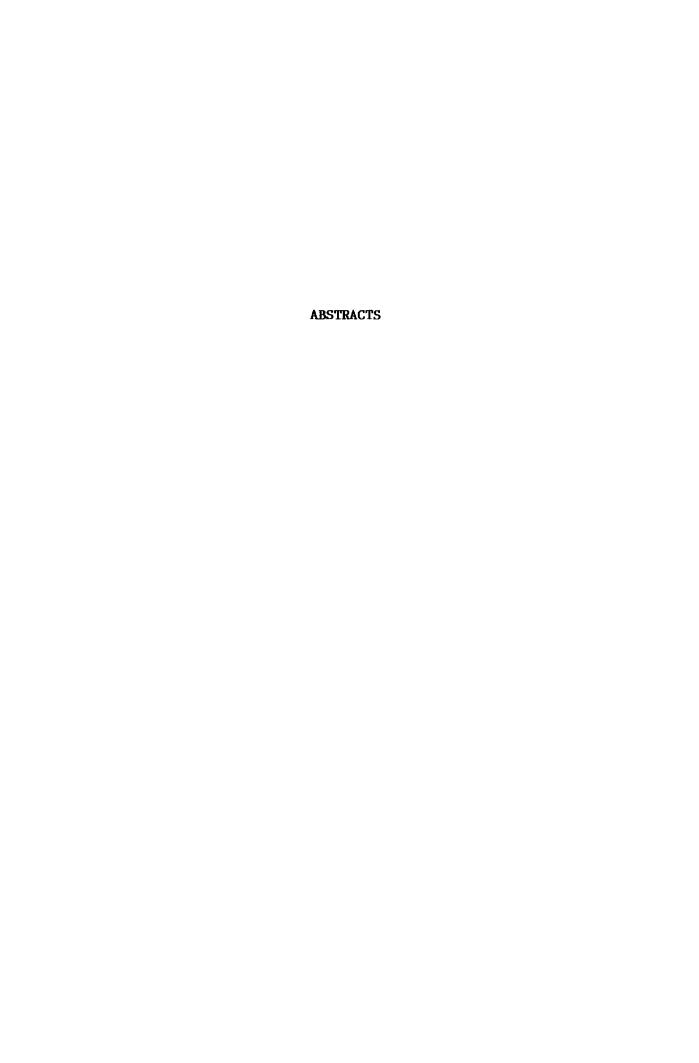
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2.40 - 3.00	31	How Y-Irradiation can Unravel Mechanisms in Free Radical Polymerizations. G.T. Russell, R.G. Gilbert, D.H. Napper (Univ. of Sydney)
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5.10 - 5.50	35R <u>Review</u>	Electric Charge Accumulation in Irradiated Films of Teflon and Mylar. V.V. Gromov (USSR Academy of Sciences)
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7.45		QUIZ: "Radiation Chemistry" Compère: Dr. G.S. Laurence (Univ. of Adelaide)

Wednesday 7th November, 1990 - Lucas Heights

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10.00 - 10.20	38	The Effect of Antioxidants on the Photochemical Degradation of a Fluorescent Whitening Agent and Tryptophan in Rigid Media. P.D. Auer, M.T. Pailthorpe, S.K. David (Univ. of N.S.W.)
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12.00 - 12.20	41	Applications of Electron Spin Resonance in Radiation Chemistry and Radiation Dosimetry - Prospects, Problems and Opportunities. J.F. Boas (Aust. Rad. Lab.)
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12.30 - 2.00		LUNCH
2.00 - 3.30		LABORATORY VISITS - ANSTO Depart ANSTO Reception



GLOBAL REVIEW OF RADIATION CHEMISTRY

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Ronald Cooper Chemistry Department University of Melbourne Vic Australia 3059

Abstract

Three important conferences on radiation chemistry topics which were held in the United States in the middle of 1990 provided an opportunity to obtain an overall perspective of recent developments in the subject and of where future advances might be expected.

The Gordon Conference on Radiation Chemistry, Newport, Rhode Island, covered the primary processes in polymers and alkanes, femtosecond investigations of electron localisation, radiation food preservation, DNA damage and photographic processes. As for most Gordon Conferences the discussion was vigorous and incisive.

Twenty five years of the Solvated Electron was attended by many of those involved in the discovery of this unique species. Papers dealt with the use being made of pulse radiolysis to solve problems in other fields of chemistry and of biology, solvation dynamics in condensed phases and electron capture in micro-domains. Notable was the number of papers in which thermodynamic considerations and energy level diagrams were invoked to explain experimental results.

The 200th Meeting of the American Chemical Society, Washington, DC, was attended by 14,235 participants organised in 30 Divisions — many of these running parallel sessions - as well as symposia on public policy and a large trade exposition. The sessions of most interest to radiation chemists were those on "Radiation Effects in Polymers". These extended over four days and dealt with almost all aspects of the subject energy transfer, dopants, crosslinking, stability, nuclear environments, composites, surface modification and technological applications. There is currently great interest in the behaviour of photo resists and radiation resists and in synthesising new ones for the manufacture of microchips. a small throughput, highly specialised field of technological importance.

More conventional radiation processing continues to be dominated by crosslinking applications but has shown the most growth in the curing of printing inks and coatings using low voltage, high current electron accelerators and in the modification of polymer surfaces by the radiation grafting of monomers containing functional groups.

RADIATION CHEMISTRY AND FOOD PRESERVATION

bу

A.J. Swallow

Paterson Research Labs. U.K.

Abstract unavailable at time of printing

Radiation Chemistry and Radiotherapy

bу

Roger F. Martin

Molecular Sciences Group, Peter MacCallum Cancer Institute, Melbourne Vic. 3000

Abstract

Radiotherapy is one of the three major modes of cancer treatment, together with surgery and chemotherapy. Surgery is the oldest treatment modality but radiotherapy dates back to the beginning of this century, not long after the discovery of radioactivity and X-rays. Not unexpectedly, radiotherapy is rather different in 1990 than it was in the early 1900s, but it is interesting to consider the nature of those advances.

The major improvements are:

- the development of high energy photon sources (20MeV compared to a few hundred MeV, and election
- the development of remote after-loading of isotope
- computerisation of treatment planning (ie. dosedelivery calculations), including integration with imaging data
- fractionation (delivery of the radiation in a series of small doses, say 25 x 2 Gy, substantially improves the balance of: tumour cell kill vs. damage to normal tissues).

With the exception of fractionation, all those developments are achievements in Engineering and Physics. From a patient stand-point, radiation chemistry has contributed little, if anything.

The purpose of this paper is to examine the possible reasons for this state of affairs and to suggest that there is nevertheless ample potential for future changes in that trend. The discussion will focus on the importance of irradiation chemistry in:

- improving our understanding of the molecular mechanisms involved in the cytotoxic effects of ionising radiation
- development of radiosensitisers and radioprotectors
- development of molecular dosimetry

The three areas are to a certain extent interdependent, and together they represent a real opportunity to improve the efficacy of cancer radiotherapy. Although the claim for such relevance of radiation chemistry is by no means novel, relatively recent developments provide some grounds for optimism.

Lowis T. Chadderton

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and

Swarnali Ghosh

Department of Chemistry
North Eastern Hill University
Shillong - 793 003
INDIA

Abstract

Ranges of 1.65 GeV Xenon ions in muscovite mica vary strongly with incident angle. This anomalous effect is due to a new kind of 'governed' particle motion - ridging - which is caused by, and exploits the stark anisotropy of the basic crystal lattice. Substantial angular differences in ridging orbits (refractive pathways) at molecular layers are the cause of a corresponding angular dependence in the effective 'nonlinear' electronic stopping power S_e , and hence in the vector range $R(\theta, \phi, E)$.

In a 4 π solid angle the surface described by range vectors \mathbf{R} of common origin and energy - spherical for amorphous condensed matter - is characteristically topographic for a crystal, due to orbital ridging, bridging, channelling, quasichannelling, blocking, and other consequences of atomic order. It is shown that this classical mechanical surface in real space, not considered previously, is the direct analogue of the quantum mechanical Fermi surface in reciprocal space for conduction electrons. Transformation of the Fermi into the classical surface with increasingly relativistic electronic mass is described geometrically. Two-beam (Bloch wave) dispersive surfaces (Fermi) become a single quasi-classical surface in the many-beam (wave) limit. Kikuchi patterns become classical star patterns. The Maxwell-Boltzmann statistics overwhelm the Fermi-Dirac.

The stable 'fundamental' particles - leptons, mesons, baryons etc. - exhibit equi-energy surfaces of one kind or the other, sometimes both, depending on mass, energy, spin, charge, and strength of interaction with crystalline condensed matter For photons (massless Bosons) and Bose-Einstein statistics a duality in scattering is also evident - from the visible to hard g-rays. For diffractive photon scattering in a crystal field a wave equation for the classic electric and magnetic field vectors now describes a corresponding structure in reciprocal space. We call this the Maxwell surface.

The 'old' Fermi surface, and the new Maxwell and classical surfaces, round off our basic understanding of the scattering of radiation generally by crystals, and symmetry is restored to the physics. There are also ramifications for solic state nuclear tracks.

Tritium Isotope Labelling of Organic Compounds catalysed by Platinum and Palladium loaded Microporous Aluminophosphates

by

Chit Than and Mervyn A. Long School of Chemistry University of New South Wales Kensington, Australia

Abstract

Tritium labelled compounds as radioactive tracers have been used routinely now for more than 55 years and are regarded as essential tools for many investigations in life sciences research. Thus there is a growing need to explore specific tritium labelling techniques. Among other techniques, catalytic exchange tritium labelling is the most attractive method to synthesize tritium labelled compounds, because the procedure is a convenient one step synthesis.

The existence of the catalytic activities for "Hydrogen Isotope Exchange Reactions" in ZSM-5, Mordenite and Y-zeolites has been recognized, and similar catalytic activities are thought to be associated to some extent with a new class of crystalline, microporous, aluminophosphates. The possibility of specific tritium labelling of various organic substrates using ALPO5, PtALPO5 and PdALPO5 catalysts was studied because there are some geometrical constraints for organic molecules absorbed into the pores of these catalysts and tritium exchange can only occur in the specific favourable position of the molecules.

Our recent work has shown that ALPOs and metal ALPOs have high catalytic activity and unique specificity for exchange between elemental tritium gas and both aromatic and branched aliphatic compounds. For example, toluene is labelled almost entirely (>90% of tritium) in the single para position. These catalysts show highly efficient activation of tritium gas and do not exhibit the simple electrophilic substitution patterns typical of acid catalysts.

The catalytic activities of PtALPO5 and PdALPO5 are compared with ALPO5 alone, reduced Pt and Pd. The tritium distribution patterns of alkanes, benzene, alkylbenzenes, polyalkylbenzenes, halobenzenes, and compounds containing a heteroatom, obtained from different metal ALPOs are highlighted.

Specific tritium labelling of organic substrates using NiALPO5 and RhALPO5, and exploration of the relation between molecular geometry and resultant tritium orientation are continuing.

RADIOLYTIC AND PHOTOLYTIC STUDIES OF LUMINESCENT DEFECTS IN IRRADIATED SOLIDS

by

Kevin Caulfield, Ronald Cooper, *John Boas and Doune Edmondson

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The University of Melbourne,
Parkville, Victoria.

*Austraiian Radiation Laboratory, Lower Plenty Road, Yallambie, Victoria.

Luminescence emissions from electron-irradiated CaO and MgO single crystals have been studied by time-resolved luminescence spectroscopy after pulsed nanosecond irradiation with 0.20 to 0.60 MeV electrons. Emissions at ~380 nm in both crystals have been attributed to oxygen displacement and show no temperature dependence between room temperature and 83 K. However a 235 nm emission in MgO exhibits a significant temperature dependence, with the appearance of two distinct displacement thresholds at 83 K.

Recent interest in radiation-induced defects in oxides has focused on more complex systems such as α -Al₂O₃ and MgAl₂O₄. A similarly unusual temperature effect has been observed in MgAl₂O₄. We propose that the higher energy threshold observed at 83 K is associated with a magnesium ion displacement process. We are presently establishing nanosecond time-resolved microwave conductivity experiments in order to confirm this theory - nanosecond pulse radiolysis will provide information about the mobility of the electronic charge carriers in these materials. These charge carriers play a crucial role in the recombination processes responsible for the luminescence observed subsequent to ionic displacement.

Picosecond laser photolysis has been used to study the fluorescent characteristics of the stable F-type centres produced in irradiated crystals. Single photon counting experiments have yielded spectra and lifetimes of electrons in traps. The excitation spectra are expected to yield information on the depth of the traps and reveal a threshold for photoconductivity.

MECHANISTIC STUDIES OF THE LUMINESCENCE FROM ELECTRON-EXCITED H₂O ICE

by

A.J. Matich¹, M.G. Bakker², T.I. Quickenden¹ and D.F. Sangster³

Abstract

When ${\rm H}_2{\rm O}$ ice is irradiated with nanosecond pulses of electrons from a Febetron 706 pulsed electron source, pulses of luminescence with a wavelength maximum around 385 nm are produced (1).

Time and temperature dependences of the luminescence have been analysed and lead to a number of mechanistic conclusions. These conclusions include information about the species involved and an explanation of the memory effects occurring in the irradiated ice.

References

(1) S.M. Trotman, T.I. Quickenden and D.F. Sangster, <u>J. Chem. Phys.</u> 85, 2555-2568 (1986).

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²Chemistry Division, Argonne National Laboratory, 9700 South Cass Ave., Argonne, Illinois, 60439, U.S.A.

Australian Nuclear Science and Technology Organisation, Private Bag 1, Menai, N.S.W., 2234.

A REVIEW OF FACTORS AFFECTING THE SELECTIVITY OF RADICAL REACTIONS

by

A.L.J.Beckwith

Research School of Chemistry,
Australian National University,
Canberra, A.C.T 2601

Abstract

Both in their modes of formation and in their reactions, organic free radicals often exhibit a high degree of chemoselectivity, regioselectivity, and diastereoselectivity. Thermochemistry has long been regarded as the dominant factor in determining the relative magnitudes of the rate constants of competing processes (i.e. the selectivity); of the various possible pathways to or from an organic radical, that which is the least endothermic or the most exothermic will be kinetically favoured.

Recent studies in our laboratories, and elsewhere, have revealed that other significant and sometimes overriding factors affecting selectivity include stereoelectronic effects, polar effects, and non-bonded interactions. An understanding of the bases of these effects allows the design of very highly selective, synthetically useful radical reactions, and the rationalisation of the outcomes of some biologically important transformations. A wide range of illustrative examples including radical reactions of vinyl monomers, carbohydrates, and amino acid derivatives will be presented.

DELAYED FORMATION OF EXCITATION IN ELECTRON IRRADIATED GASES

by
Manuela Burgers and Ronald Cooper

Department of Chemistry, The University of Melbourne, Parkville, Victoria.

Activated species are produced in irradiated systems by so-called direct and indirect mechanisms. the high energy particle (e-, p, etc.) or photon (X, γ) may directly interact with the molecular modes of the target system producing ionisation, electronic excitation and secondary electrons. This process is direct and fast. The secondary electron distribution (degradation spectrum) can further interact with the target medium and produce more ionisation and excitation until the system has become thermalised. These processes can be observed by fast response emission spectroscopy and electrical conductivity methods.

In high pressures of rare gases, two distinct time zones can be observed for the production of electronic excited states; a fast process has been shown to be due to both direct and subexcitation electron effects; a slower dose dependent process has been interpreted as being due to ionic recombination: $M^+ + e^- \longrightarrow M^*$.

Recent measurements by us have shown that the kinetics of formation and decay of this slow emission cannot be due to ion recombination. Ion-electron recombination is too slow under these conditions and the decay kinetics are not second order.

The fluxes of secondary electrons in high dose rate systems may be sufficiently high to cause excitation of some long lived excited states back up to higher levels which can then relax by emission down to the same long lived states. This recycling-excitation process can occur until the electron energy falls to the threshold for the particular excited state. In the case of neon this is of the order of 1.5 to 2.5 eV. The delayed emission will persist whilst the electrons have sufficient energy to re-excite the 1s levels of neon to the 2p levels and also whilst the population of 1s states is not depleted by emission or reaction with impurities. This model is being tested by experimental measurements and by theoretical calculation.

Evidence has also been discovered which indicates that this re-excitation process may also occur at very low pressures giving apparently too low values for emission lifetimes in these well characterised systems.

ELECTRON-ION RECOMBINATION IN NOBLE GASES

by

Ravindra Bhave, Ronald Cooper, Roger Van Sonsbeek and Kevin Caulfield
Department of Chemistry, The University of Melbourne,
Parkville, Victoria.

The recombination of charged particles in gases was first studied by Thomson and Rutherford in 1896. Their investigation found that conductivity of a gas exposed to X-rays is due to the presence of ions and concluded that ion-ion recombination must occur. They denoted α as a second-order rate coefficient for this process.

More recent study reveals that the recombination is a two step process i) Diffusion of the positive and negative ions or electrons and ii) Charge neutralization. At low gas pressures the charge neutralization becomes rate controlling and the recombination coefficient α is proportional to the pressure of bulk gas. Further studies at high pressure have shown that the total recombination coefficient a is a combination of two (α_2) and three body processes (α_3) ,

 $\alpha = \alpha_2 + \alpha_3$ N where N is bulk gas number density.

There has been little investigation of the effect of temperature on recombination rate. It is predicted in theory that α_2 , the two body rate coefficient is independent of temperature since the rate controlling process is the decay of excited states. The three body rate coefficient α_3 should have a negative dependence on temperature since α_3 depends on collisions of the encounter pair with the bulk medium.

Electron-ion recombination in noble gases is studied by using a pulse radiolysis technique involving a Febetron as a source of an electron pulse and change in microwave conductivity as a means to detect the ion concentration in various gases under study at different pressures and temperatures. The results obtained are compared with predictions from existing theories developed for explaining electron-ion recombination.

THE RADIATION CHEMISTRY OF "BIOPOL"

by

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Abstract

Poly(hydroxy butyrate) and copolymers with hydroxy valerate have in recent years been marketed by ICI under the trade name "Biopol". Some interesting features include its production, biodegradability and biocompatibility.

$$\left(\begin{array}{ccc}
R & O \\
I & II \\
CH - CH_2 - C - O
\end{array}\right)_{\Pi}$$

R = CH, hydroxy butyrate = C.H. hydroxy valerate

"Biopol" is one of a new generation of polymers in that it does not rely on the petrochemical industry, but is produced by bacteria as an energy storage material under appropriate conditions. In soil, sewerage, etc. it is rapidly broken down once again by bacteria.

The limited amount of published work on the radiation chemistry of "Biopol" is mainly involved with the changes in the mechanical properties upon irradiation. The present investigation includes the use of gas chromatography by which the gases are identifies and the G values obtained. Molecular weight changes using Gel Permeation Chromatography have been measured and the amount of permanent chain scission and crosslinking obtained. The identification and quantification of the radicals produced has been done using Electron Spin Resonance while the end groups appearing upon irradiation have been identified by Nuclear Magnetic Resonance. By bringing all these results together a possible mechanism for the degradation of these polyesters will be suggested.

PHOTODEGRADATION OF PVC SYSTEMS

by

David J.T. Hill, Francing Kicksey. James H. O'Donnell and Poter J. Posety

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Abstract

Poly(vinyl chloride) is one of the most important commercial thermo-plastics and has many applications, including outdoor use. A variety of copolymers blends and composites of PVC are being developed by the polymer industry to extend the range of material properties and applications. The present study of the photodegradation of PVC was designed to provide a basis for examination of more complex PVC systems.

PVC film was prepared by dissolution and solvent casting after purification by reprecipitation and rigourous removal of the solvent (heating in vacuum at 100 °C: above Tg)

UV-visible spectra of the unirradiated cast films showed the presence of oxidized THF residual solvent, except after rigourous drying. These dried films had developed a purple colouration and showed evidence of polyene formation from absorbances in the range 250 to 420 nm. The intensities of the polyene absorbances increased with irradiation and were observed in all samples. The degradation appeared to be sensitized by the presence of initial polyene structures.

IR spectra showed the formation of carbonyl and hydromyl groups during irradiation, which could be correlated with the absorbed dose. Molecular weights, measured by GPC, decreased with irradiation. Some chain scission had also occurred during the rigourous drying procedure.

ELECTRON ENERGY LOSS IN IRRADIATED MOLECULAR GASES

by

Ravindra Bhave and Ronald Cooper

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Primary energy deposition processes in irradiated systems involve the degradation of an initially high energy particle or photon to thermal energies. This usually occurs before conventional chemical processes can take place and hence does not interfere with radiation chemical experiments designed to obtain rate constant data for thermal reactions. The use of ultrafast pulse radiolysis techniques has recently enabled kinetic studies of many ionic and free radical processes to be undertaken but the possibility exists that primary radiolytic processes may interfere with such studies.

The slowest of all the primary radiolytic processes is the establishment and cooling of the secondary electron spectrum. This process may conveniently be studied in ionised gases since the conductivity depends on the number of electrons present as well as their mobility. Crucially, the mobility is dependent on the mean energy of the electrons and so provided that the loss of electrons is negligible during the experiment then the change in conductivity with time can be directly related to the rate of cooling of hot secondary electrons.

Using helium, where the thermalisation time is well known, the effects of addition of small amounts of molecular gases in increasing the thermalisation rate can be observed. Using nanosecond pulse radiolysis techniques together with time resolved microwave conductivity methods, this process can be observed. The results to date show that the distribution of electron energies is initially non thermal and also non maxwellian in distribution. This latter is shown by the kinetics of electron energy decay which cannot be fitted to any conventional kinetic order. However, in the case of systems with a trace of added molecular gas, e.g. H_2 , CH_4 , CO_2 , N_2 the kinetics eventually become pseudo first order. This enables a time to be measured for the attainment of a maxwellian type distribution, further, the pressure dependence of the pseudo first order rate constant will give a two body thermalisation rate constant.

A SEARCH FOR ELECTROCHEMICALLY INDUCED COLD NUCLEAR FUSION

Ьу

T.I. Quickenden, R.W. Brunning and T.A. Green

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Abstract

A number of long term experiments were carried out on the electrolysis of heavy water using palladium cathodes in order to search for anomalous heat releases which might be attributed to cold fusion of deuterium. Cell temperatures were monitored continuously with duplicate thermistors on independent circuits and cell voltages and currents were also continuously recorded. Total cell running times exceeded 50,000 hours.

Various electrode preparations and electrolysis conditions were used in order to search for the appropriate conditions for anomalous heat production. The results of these experiments will be reported. o_2 (A³) $u \longrightarrow x^3$ $u \longrightarrow x^3$ HERZBERG I EMISSION FROM UV IRRADIATED H₂O AND D₂O ICES

by

A.J. Matich , M.G. Bakker , C.G. Freeman and T.I. Quickenden

Abstract

Previously reported (1) emission bands from UV excited ice have now been more highly resolved and examined in D_0O as well as H_0O ice.

Three dimensional profiles of the excitation and emission spectra will be presented. It will be shown that the series of bands thus obtained is consistent with the Herzberg series of molecular oxygen referred to above. The absence of detectable wavelength shifts when D was substituted for H ruled out emission from excited OH and other hydrogen containing water fragments.

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THE USE OF NOVEL ADDITIVES IN RADIATION GRAFTING

by

Paul Dworjanyn University of New South Wales,

The role of additives is important in radiation grafting processes since the inclusion of appropriate materials in a grafting solution can enhance the grafting yields. Thus the radiation dose to achieve a particular percentage graft can be lowered in the presence of additives.

This paper will discuss the use of a selection of novel additives to enhance grafting yields with polypropylene as the model substrate. The use of both ionising and non-ionising radiation sources will be considered.

ELECTRON SPECTROSCOPIC STUDIES OF THE ADSORPTION OF CARBON TETRACHLORIDE ON OXIDISED Ni (110)

bу

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Abstract

The adsorption of CCl $_4$ on oxidised Ni(110) at 300 K was investigated using vibrational electron energy loss spectroscopy (EELS) and Auger electron sprectroscopy (AES). Adsorption was found to be dissociative with a nickel-chlorine stretching loss peak in the EEL spectrum at $29.8\pm 8~{\rm cm}^{-1}$.

In the case of adsorption of CCl $_4$ on a thin, continuous layer of nickel oxide, AES showed that no carbon was present at the surface. Mass spectrometric analysis of the gas resulting from exposure of nickel oxide powder to CCl $_4$ vapour indicates that the adsorbed carbon is oxidised and desorbs as CO and CO $_2$.

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REDOX CHEMISTRY OF SOME TETRA-AZA MACROCYLCIC COMPLEXES

by

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and

School of Physical Sciences
The Flinders University of South Australia
ADELAIDE, South Australia

Abstract

The chemistry of tetra-aza macrocyclic complexes is considerably modified by the presence of pendant arms on the macrocycle which can interact with the metal ion in the macrocycle. Complexes of cobalt, nickel and copper with tetrahydroxyethyl cyclens have been synthesized. In these complexes the pendant arms terminate in hydroxy groups.

The stability constants and spectra of the complexes have been measured over a range of pH and the redox behaviour investigated by cyclic voltammetry and pulse radiolysis. The spectra and properties of the one-electron reduced species are reported.

POLYMERISATION OF MICROEMULSIONS USING GAMMA-RADIOLYSIS

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Sydney, N.S.W., 2006, Australia

Abstract

The effects of a wide range of dose rates and relaxation after removal from source on the polymerisation rate, particle size distribution and molecular weight distribution were investigated for styrene-in-water microemulsions of hexadecyl trimethyl ammonium bromide (CTAB, a cationic surfactant) and hexanol (a co-surfactant of CTAB). It was observed, amongst other things, that in contrast to normal emulsion polymerisation, (i) the polymerisation rate shows only two intervals, increasing to a maximum before falling; (ii) latex particles are reasonably small (number average radius varied from 7 to 11 nm) and contained only one or two polymer chains of a relatively high molecular weight ($<M_W>=3$ to 5×10^6); and (iii) the number of latex particles and the average molecular weight of the chains was found to be insensitive to the dose rate at low dose rates, whilst showing a dependence at higher values. Note however, that the polymerisation rate showed a strong dependence over the entire range of dose rates.

Extensive Monte Carlo simulations of the polymerisation microemulsion based upon the theory of time-dependent stochastic processes have been performed. In these simulations, latex particles are formed directly from microemulsion droplets following the entry of oligomeric free radicals into the droplets. Surfactant and monomer are supplied to growing latex particles from the microemulsion phase which continues to exist throughout the polymerisation. The amount of surfactant and monomer remaining to the microemulsion determines the number of actual droplets at any given time, which apparently are prosent in sufficiently large numbers to ensure only one or two chains per latex particle. In addition, at low dose rates, polymer chain termination occurs predominately by chain whilst at higher dose rates, chain termination transfer. increasingly by bimolecular combination.

SOME ADDITIONS TO THE PULSE RADIOLYSIS FACILITY

by

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Abstract

A "slow" stopped-flow device has been built to allow pulse radiolysis experiments to be carried out on solutions which are unstable over a period of ten seconds to a few minutes. The injection system is electronically controlled and can be operated from outside the accelerator cell. It can also be used for the controlled changing of more normal solutions in the pulse radiolysis cell.

The conversion of the pulse radiolysis data-collection and analysis system to operate on MS-DOS based computers will be demonstrated. The new system has a number of features missing from the old DEC system and users should find the new file format particularly useful. Data are now stored in files in standard ASCII format and so can be read and edited in most DOS word-processors as well as the LHKDATA program itself. Editing and data handling have been improved and an on-line help facility provided.

The data can also be used as input to commercial programs such as MS CHART for the production of printed graphs for presentation. Subsidiary programs provide for the production of the spectra of transient species from a series of experiments at different wavelengths.

The system is being demonstrated so that suggestions and advice from potential users can be incorporated in the final version.

STUDIES OF OXIDATIVE DEGRADATION OF POLYMERS INDUCED BY IONIZING RADIATION

by

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<u>Abstract</u>

Early studies of polymer radiation chemistry focused primarily on experiments conducted under inert atmosphere. However, most important applications of polymers in radiation environments involve exposure to atmospheric oxygen, in which case very different (often much larger) material property changes result. Polymer radiation effects in the presence of air are characterized by complicated phenomena such as dose-rate effects and post-irradiation degradation. These time-dependent effects can be understood in terms of two mechanisms: 1) features of the free radical chain-reaction chemistry underlying the oxidation, and 2) oxygen diffusion effects. A modulus profiling device has been developed with which heterogeneous degradation, resulting from oxygen diffusion effects, has been extensively studied. Chemical-kinetic schemes have been derived which allow successful material lifetime predictions from short-term high-dose-rate experiments. Low molecular weight additives, which act either as freeradical scavengers or else as energy-scavengers, are effective as stabilizers in radiation-oxidation environments. Non-radical oxidation mechanisms, involving species such as ozone, can also be important in the radiation-oxidation of polymers.

Session V Tuesday 9.00 - 9.40 a.m.

RADIOLYSIS OF POLY (ACRYLONITRILE) S

by

D.J.T. Hill, A.P. Lang, J.H. O'Donnell and P.J. Pomery
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Abstract

Over a period we have investigated the gamma radiolysis of several copolymers of styrene and other monomers, including the copolymers of styrene with methacrylic acid and methyl methacrylate. The homopolymers of these comonomers display a propensity to undergo scission on radiolysis, but polyacrylonitrile has been reported to undergo crosslinking, as does polystyrene. The copolymers of acrylonitrile and styrene can be characterized by ¹³C NMR and their microstructure is well known.

In this paper a study of the radical intermediates formed on gamma radiolysis of polyacrylonitrile and several of its copolymers with styrene will be reported at 77 and 300 K. Photobleaching and thermal annealing have been used to identify the major radicals and to study their reactivity. The molecular weight changes induced by radiolysis of the copolymers have also been investigated. The yield of radicals and of crosslinking and scission will be interpreted in terms of the protection effect provided by styrene in these systems.

AN INVESTIGATION OF RADIATION-INDUCED STRUCTURAL CHANGES IN NITRILE RUBBER.

D.J.T.Hill, J.H.O'Donnell, M.C.S.Perera and P.J.Pomery

Polymer Materials and Radiation Group, Department of Chemistry, University of Queensland, Q 4072, Australia.

Abstract

Nitrile rubber, a copolymer of butadiene and acrylonitrile, undergoes crosslinking during exposure to high energy radiation. However, very few studies have been reported on the radiation yields and structural changes. A cyclisation reaction involving nitrile groups, was reported from an infrared spectroscopic study, but the evidence was inconclusive.

The molecular structure of nitrile rubber is complex on account of the different possibilities for polymerisation of the butadiene units, and has not yet been completely elucidated. A 2D $^{1}\mathrm{H}$ - $^{13}\mathrm{C}$ correlation was carried out in the present work, to complete the assignments of the $^{1}\mathrm{H}$ and $^{13}\mathrm{C}$ NMR resonances. From the $^{13}\mathrm{C}$ NMR spectra it was apparent that the nitrile rubbers with less than 33% acrylonitrile contain acrylonitrile groups almost entirely as isolated monomer units and therefore the cyclisation reaction previously proposed cannot be significant.

ESR was used to measure the concentrations of radicals formed during irradiation at 77 K. The changes in the radical concentration during thermal annealing assisted the identification of the radicals.

Solid-state ¹³C NMR and FTIR were used to study the structural changes which takes place on irradiation. Cross-polarisation, dipolar-decoupling and magic angle spinning were used at elevated temperatures to narrow the resonances in the solid-state NMR spectra, which were resolved by simulation using appropriate line widths and shape factors. The yield of crosslinking was determined directly from these spectra. Both NMR and FTIR indicated changes in the nitrile groups and double bonds.

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RADIATION INDUCED THERMAL DEGRADATION OF POLY(α -METHYL STYRENE)

by

R.W Garrett, D.J.T. Hill, <u>T.T. Le</u>, J.H. O'Donnell and P.J. Pomery.

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Abstract

Poly(a-methyl styrene), PaMS, has a much lower ceiling temperature (61°C) than other similar polymers, for example polyisobutylene 175°C, poly(methyl methacrylate) 196°C or polystyrene 395°C. Therefore, PaMS has the potential to undergo radiation induced scission at relatively low temperature.

At temperatures below 80°C the polymer undergoes scission, but no significant depropagation is observed. However, at 100°C radiation induced depropagation is observed to occur, at a measurable rate, with a monomer being the only product of the unzipping reaction. The rate of depropagation increases as the temperature rises to the glass transition temperature, 180°C. At this temperature, in the absence of radiation, no thermal decomposition takes place. However, if the temperature is raised to 220°C, thermal decomposition does occur spontaneously.

The loss of monomer and the resultant decrease in weight of the polymer complicates the measurement of G(-M) and G(S), and requires that the absorbed dose be calculated allowing for the loss in mass. If the zip length (z) is large, and comparable with the degree of polymerization, chain-end effects cannot be neglected. In these cases z and G(S) must be determined using a Monte Carlo simulation technique.

In this paper the measurement of G(-M), G(S) and z will be discussed for studies of the radiation induced thermal degradation of PaMS in the temperature range $30-180^{\circ}$ C.

RADIATION CHEMISTRY OF POLYMERS AND MODEL COMPOUNDS STUDIED BY NEW PICOSECOND AND NANOSECOND ELECTRON, ION, AND SR PULSE RADIOLYSIS SYSTEMS

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Abstract

A number of papers on radiolysis of polymers and model compounds have been published for a long time. Recently main reactive intermediates in radiolysis of polymer solutions and polymer films such as electrons, ions, excited states and radicals have been measured clearly even at room temperature by using pulse radiolysis systems. Especially very clear absorption spectra of main reactive intermediates have been observed for irradiated polystyrene (1), resist materials (2), polysilanes (3), polygermanes (4), polyolefins (5) and their model compounds (5).

Very recently absorption of electrons and the charge resonance bands of dimer cations in infra-red region have been observed at room temperature (6). The comparison of decay behavior of electrons with radical cations are easily studied now. The reactions of electrons with solute molecules and geminate processes have also studied.

For the formation and decay processes of reactive intermediates including geminate recombination on picosecond time scales have been studied now by new twin linac picosecond pulse radiolysis system "LL Twin LINAC System" (7).

Very recently nanosecond ion beam pulse radiolysis (8) and picosecond synchrotron pulse radiolysis (9) studies on polystyrene, plastic scintillators, PMMA and polyolefin model compounds have also studied. Clear LET effects have been observed on transient species in radiolysis of model compounds of polyolefins(10).

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AN EPR STUDY OF FREE RADICAL BEHAVIOUR IN IRRADIATED DRAWN POLYETHYLENE.

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ABSTRACT

EPR is being used to study the radicals formed in γ -irradiated drawn polyethylene and their behaviour upon sample heating and in the presence of additives such as acetylene and butadiene. Irradiation is known to improve the creep properties of polyethylene by inducing crosslinking of the polymer network. This process is enhanced in the presence of sensitisers such as acetylene. Our objective is to obtain a fundamental understanding of how the effects of high energy radiation are influenced by the morphology changes induced by drawing. Subsequently we will be able to determine the optimum condition for property improvement.

Two ranges of samples are being investigated. One consists of a range of draw ratios from 1 to 30 all drawn under as near identical conditions as possible from a common stock of polyethylene film. The other consists of samples of ultra high modulus polyethylene fibre, all with the same draw ratio of 20 but with varying physical form (multifilament and monofilament), and varying molecular weight from 10⁴ to 10⁶. The higher molecular weight samples were made by the gel spinning method, the lower molecular weight samples were made by melt spinning.

The rate of free radical decay was found to be dependent upon a number of factors such as molecular weight, draw ratio and physical form (monofilament vs multifilament).

For example the rate of decay at 313 K increases with draw ratios in the order 1 > 30 > 20 > 10.

The minimum in decay rate observed between draw ratio 1 and 10 can be correlated to major morphological changes which occur in this region.

TEMPERATURE DEPENDENCE OF THE RADIATION DEGRADATION OF POLY(METHYLMETHACRYLATE) AND POLY(PHTHALALDEHYDE)

by

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<u>Abstract</u>

The yield of scission, G(S), is underestimated if polymers are irradiated at elevated temperatures, when depropagation occurs [1]. The aim of the present work is to measure the temperature dependence of (1) the molecular weight distribution and (2) the mass loss of selected polymers during irradiation. Poly(methyl methacrylate) has been studied as a model polymer which depropagates above about $150^{\circ}C$ and also undergoes scission exclusively. Polyphthalaldehyde is of interest because of its potential application as a photoresist in the microelectronics industry. Experimental measurements on these polymers and comparison with theory enables estimates of the true G(S) and of the zip length for depropagation.

The irradiations were carried out in the GATRI facility at Lucas Heights using an aluminium block heater and a high vacuum system so that the monomer was removed continuously from the sample. Mass losses were determined by direct weighing and molecular weights were measured using gel permeation chromatography.

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SURFACE MODIFICATION OF EPDM RUBBER

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Abstract

Many properties and associated applications of polymers depend upon the status of the polymer surface. They include adhesion, chemical resistance, wettability, permeability, flame retardancy, bio-compatibility, etc. Therefore, surface modification of a particular polymer having optimum bulk properties is an efficient way to make it suitable for a special application. For example, surface commodity polymers may be a cost-effective alternative to expensive specialty materials.

Radiation-induced grafting has been found to be the most efficient method for surface modification. For many years this method has been used to develop biomaterials by grafting monomers for biological applications. They include 2-hydroxyethylmethacrylate (HEMA), acrylamide (AAM), and N-vinylpyrrolidone (NVP) into for example, the surface of silicone rubber and other polymeric supports [1-6]. The oil-resistivity of ethylene-propylene and butadiene-styrene elastomers has been modified by grafting with acrylic monomers [7].

Rubbers based on ethylene and propylene (i.e. EPR and EPDM) are widely used due to their long service life, chemical resistance, biostability and excellent mechanical properties. However, they suffer from low surface tension, poor wettability and hydrophilicity and therefore low biocompatibility.

The present work describes the grafting of polar and biocompatible monomers such as HEMA, AAM and NVP into the surface of EPDM rubber using $^{60}\text{Co-}\gamma$ radiation. Grafting parameters such as radiation close and doze rate, monomer concentration, type and concentration of inhibitor, and rubber structural factors have been investigated. Changes in chemical composition, surface tension, biocompatibility, thermal stability and oil resistance of the grafted EPDM's are described.

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RADIATION POLYMERISATION IN ORDERED ASSEMBLIES

by

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*

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**

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Abstract

The radiation-induced homopolymerisation of biphenyl acrylate has been studied from a kinetic and mechanistic standpoint. Polymerisations were carried out with dimethyl formamide as the solvent for both the monomer and resulting polymer. Examination of the experimental data, together with characterisation of the polymeric products leads us to the conclusion that the monomer is present in solution in a "semi-ordered" assembly. Such ordering influences the nature of the polymerisation and the properties of the products. Evidence to support this view has been provided by a pulse radiolytic study of the biphenyl acrylate -dimethyl formamide system.

THE USE OF γ -RADIATION IN THE INVESTIGATION OF FREE RADICAL KINETICS IN EMULSION POLYMERISATION

by

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and

David F. Sangster

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Abstract

An emulsion polymerisation system is heterogeneous and may contain up to three separate physical phases: a dispersive medium, commonly water (containing a small amount of the sparingly water-soluble monomer and, at times, surfactant micelles), emulsion droplets (containing monomer) and latex particles (consisting of polymer, monomer and surfactant, which acts as a surface stabiliser). Either an oil-soluble or a water-soluble initiator is added to generate, by thermal decomposition, the free radical species which then initiate polymerisation in the latex particles [1].

An alternative method of free radical generation is via the application of γ -radiation. γ -radiation interacts with materials, like water, to cause ionisation and electronic excitation. The electrons produced, their adducts with other substances, the parent positive ion and the radical pairs formed by homolysis of excited molecules are all free radicals which can initiate polymerisation.

The advantage of γ -radiation over chemical initiators is its ability to provide a discontinuous radical flux during a polymerisation experiment. Whereas chemical initiators are present throughout polymerisation, it is a simple procedure to remove an emulsion sample from a γ -radiation source. The resulting rapid change in free radical production rate provides more kinetic information than is available from the more common steady state experiments.

The use of γ -radiation experiments to elucidate mechanisms of free radical polymerisation [2], with a special emphasis on termination processes [3], will be discussed in the paper. Further, an outline of the mysteries of radiation chemistry, with respect to emulsion polymerisation, will be presented. The solutions to these problems would greatly assist the polymer chemist in dealing with the complexities inherent in the free radical kinetics of emulsion polymerisation.

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HOW γ -IRRADIATION CAN UNRAVEL MECHANISMS IN FREE RADICAL POLYMERIZATIONS

Gregory T. Russell, Robert G. Gilbert and Donald H. Napper School of Chemistry, The University of Sydney, N.S.W., 2006, Australia.

Free radical polymerizations involve the simultaneous presence of free radical polymer chains of all degrees of polymerization that are possible under the prevailing reaction conditions. Because of this, pinpointing the rate-determining reactions in high-conversion free radical polymerizations is a non-trivial exercise: such an abundance of species is present that it is very difficult to specify exactly which lengths of free radicals are involved in the reactions that primarily determine the overall rate of polymerization. However, through the use of γ -irradiation considerable progress towards fully unraveling this puzzle has been made. The basic scrategy in this regard has been to use γ -radiation to initiate a polymerization, and then to remove the polymerization vessel from the γ -source. During the ensuing relaxation into an out-of-source pseudo-steady state, the termination reaction is to the fore. Monitoring the kinetics of polymerization during this period enables subsequent modeling of these kinetics to be carried out, and in this fashion much headway can be made in understanding the intricacies (alluded to above) of the termination reaction.

The broad aim of this work is therefore to forge towards an understanding, at a molecular level, of termination in high-converion polymerizations. Preliminary investigations in this regard have already been reported: these utilized experimental data from the $(\gamma\text{-initiated})$ emulsion polymerization of styrene. A feature of this previous work was the use of a model that accounts for, albeit very coarsely, the chain length dependence of the termination rate coefficient. The present work seeks to build on this initial work by accounting for more fully the chain length dependence of the termination rate coefficient. It will be shown that through considered analysis of γ -relaxations, a precise microscopic picture of termination in high-conversion free radical polymerizations has emerged.

¹ M.E. Adams, G.T. Russell, B.S. Casey, R.G. Gilbert, D.H. Napper and D.F. Sangster, Bimolecular Termination Events in the Seeded Emulsion Polymerization of Styrene, Macromolecules, in press, 1990.

THE USE OF HIGH ENERGY RADIATION PROCESSING

FOR PROCESSING OF NOVEL BIOMATERIALS

M V MARKUS

ICI RESEARCH GROUP NEWSOM STREET ASCOT VALE 3032

ABSTRACT

High Energy radiation generally interacts with polymers in two basic manners, both resulting from excitation or ionisation of atoms in the polymer by the high energy source. Alterations in molecular structure of the polymer as a result of these interactions appear as changes in the chemical and physical properties.

The two mador effects of high energy radiation on polymers are:

- Chain scission, occurring as a random rupturing of bonds, resulting in reduction of the molecular weight of the polymer;
- * Crosslinking of polymer molecules, resulting in the formation of a three-dimensional polymeric network.

Usually both of these mechanisms occur, but frequently one mechanism will predominate with a specific polymeric substrate.

As a result of chain scission, very low molecular weight fragments, gas evolution and unsaturated bonds may appear. Crosslinking generally results in an initial increase in tensile strength, while impact strength decreases and the polymeric substrate becomes brittle. However, if during or immediately after exposure of polymeric materials to high energy radiation unsaturated monomers are present, direct or indirect radiation—initiated grafting will occur. Thus, by these methods, new polymeric substances (or new forms of polymers) may be synthesized or existing polymers modified,

Using this simple and relatively cheap processing of polymeric substrates, many final products find end use in:

- Medicine as * implements, * implants or * instruments
- II Analytical chemistry as * chromatographic supports
- Pharmaceutical products as * controlled drug delivery systems,
 * supports for production of mammalian cells,
 - * microbiologically free synthetic skin or * supports for immobilization of enzymes.

MOBILE CHARGE CARRIERS IN PULSE IRRADIATED POLYMERS AND MOLECULAR AGGREGATES

by

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Abstract

Many of the materials of interest in applied radiation chemistry or radiation biology tend to be heterogeneous in nature. This makes them often difficult to probe using conventional pulse radiolysis techniques, especially if one is interested in a specific microscopic region within the sample. The radiation induced conductivity change can be studied by measuring changes in the microwave absorption using the time resolved microwave conductivity technique (TRMC) [1-3]. With this method there are no polarization problems and no requirements of good contacts as for a conventional DC conductivity technique. In this way conductivity measurements can be carried out in powders, fibers, films and blocks of polymers or molecular aggregates.

Results will be presented on charge migration in several polymers, such as polytetrafluoroethylene (PTFE), ultra high molecular weight polyethylene (UHMW-PE), and columnar aggregates of peripherally octa-n-alkoxy substituted phthalocyanines (PC). In these materials mobile charge carriers are observed with mobilities of the order of 10^{-4} m²V⁻¹s⁻¹ [4-6]. In UHMW-PE and PTFE the rapid charge migration is found to persist for approximately 20 ns after pulse irradiation at room temperature. In PC the charge carrier lifetime is found to be much longer and strongly dependent on the length of the alkoxy chains.

Experiments with thin films and fibers of UHMW-PE with the polymer chains parallel or perpendicular to the electric component of the microwave field indicate an anisotropy in the conductivity. Along the chains the conductivity is found to be at least a factor of 30 larger than perpendicular to the chain, indicating very rapid one-dimensional conduction of charge.

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CROSSLINKING OF POLYOLEFINS BY HIGH ENERGY IRRADIATION

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ABSTRACT

Polyethylene has been crosslinked by both irradiation and chemical methods on a commercial scale for many years. The process leads to an improvement in properties of valuable practical advantage in the electrical insulation and blown foam industries.

This lecture will only deal in detail with crosslinking by irradiation. The effects of irradiation are of course, dependent on a number of factors; chemical structure and sample morphology are examples of For example although isotrope polyethylene interest. undergoes predominantly crosslinking when irradiated in an inert atmosphere, polypropylene undergoes roughly equivalent amounts of chain scission and crosslinking under the same conditions, leading to a deterioration in some key mechanical properties. Also drawn polyethylene is more prone to chain scission than isotropic polyethylene such that irradiation in vacuum or air leads to some loss of tensile strength, a key property of drawn fibres and tapes. Thus the advantages which might be gained by irradiating drawn polyethylene, such as improvement in performance, are more than counter balanced by the deleterious effect.

These are problems which a fundamental understanding of the irradiation process, particularly the effects of chemical structure, sample morphology and the presence of additives, may help to solve. In addition to a survey of irradiation crosslinking in general, the lecture will focus on studies related to these issues.

ELECTRIC CHARGE ACCUMULATION IN IRRADIATED FILMS OF TEFLON AND MYLAR

рy

V.V.Gromov

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Abstract

It was obtained the non-uniform spatial disrtibution of positive electric charge in the dielectrics (mylar and teflon which are widespread in space technique) under irradiation with protons of 0,8 MeV energy. The negative charge region appears in addition to the positive one formed by injected protons and compensates it partialy. The location of positive charge agrees satisfactionary with protons path in the materials.

MEDICAL APPLICATIONS OF RADIATION CHEMISTRY WITH SOME REFERENCE TO ANSTO'S PROPOSED MEDICAL CYCLOTRON

by

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Abstract

The Biomedicine & Health Program at Ansto is committed to promotion of multi-disciplinary research and development efforts with a focus on several medical applications of radiation. Cooperation within the Lucas Heights Research Laboratories with universities through Australia, and with industry are being enhanced. Ansto's National Cyclotron Facility located at the Royal Prince Alfred Hospital, Sydney, will be commissioned July 1991. The 30 MeV H cyclotron will be utilised for routine production of medical radionuclides to be distributed by Australian Radioisotopes, and as the generator of short-lived positron emitting radionuclides utilised for biomedical research and clinical PET.

Radiation chemistry considerations are an integral component with regard to: (1) target stability under high beam current conditions required to produce multi-curie quantities of medical radionuclides; (2) the on-line preparation of precursors required for the rapid synthesis of radiopharmaceuticals; (3) self-radiolysis of high specific activity and no-carrier-added radiopharmaceuticals; and (4) in vivo microdosimetry of radioactivity administered for diagnosis or therapy.

Specific examples and program plans will be discussed.

STUDY OF THE INTERACTION OF OXYGEN WITT PHOTOEXCITED STATES OF SOME DNA-BINDING DRUGS

by

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#Molecular Sciences,
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A series of compounds were synthesised by the Hoechst Pharmaceutical Company in the early 'seventies and found to bind strongly to the minor groove of the DNA helix. The fluorescence of these drugs is strongly enhanced upon binding to DNA and has resulted in their widespread use as dyes for the visualisation of both isolated and cellular DNA in biochemistry.

The derivative 'Hoechst 33258' is noted for its ability to sensitise the production of single strand breaks of DNA containing covalently-substituted halogen atoms. The mechanism for the initiation of dehalogenation which precedes the oxidative degradation of the DNA is unknown. Measurements of the photosensitised yields of production of the singlet oxygen and superoxide species are reported for some of these Hoechst derivatives. These results are compared with the yields of production of both species upon binding to DNA. It is believed that the photoexcited Hoechst moiety may either surrender an electron to oxygen or when bound to halogenated DNA, facillitate intra-molecular electron transfer to the substituted halogen atom. Thus, the halogen atom is lost as the corresponding halide ion and the carbon-centred radical of the DNA base rearranges to produce a strand break in the DNA sugar backbone. The results of this study shed some light on the mechanism by which the excited state of the drug mediates the homolytic cleavage of the halogen atom.

THE EFFECT OF ANTIOXIDANTS ON THE PHOTOCHEMICAL DEGRADATION OF A FLUORESCENT WHITENING AGENT AND TRYPTOPHAN IN RIGID MEDIA

by

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Abstract

Wool which has been treated with a fluorescent whitening agent (FWA) to attain a commercially acceptable whiteness, suffers from accelerated and photosensitized yellowing compared with untreated wool when exposed to UV radiation [1]. The source of this yellowness in both treated and untreated wool is thought to be the degradation products of tryptophan (TRP), a photolabile amino acid residue of wool keratin, formed by the reaction of TRP with singlet excited oxygen ($^{1}O_{2}$) [2]. $^{1}O_{2}$ is thought to be generated when triplet oxygen quenches the triplet excited state formed by the FWA when near-UV radiation is absorbed [3].

The coloured photoproducts of TRP are thought to be produced via hydroperoxide intermediates [4],[5]. These reactive intermediates have been successfully neutralised by the use of antioxidants [6], which are widely used in the p'astic [7] and food industries [8]. It is thought that these photoprotective agents should have a beneficial effect on reducing the accelerated photoyellowing of FWA-whitened wool.

As an adjunct to the study of the effect of antioxidants on the photoyellowing of FWA-whitened wool, the effect of antioxidants on the degradation of a FWA (Uvitex NFW; Ciba-Geigy) was studied. Various polymer films (polyvinyl alcohol, methyl cellulose, gelatine) were used to encapsulate the FWA and to simulate, as closely as is possible, the rigid medium of the wool fibre. The effect of antioxidants on the degradation of TRP in rigid media has also been studied.

These studies have elucidated the effects of both substrate and antioxidants on FWA degradation, and the effects of substrate and antioxidants on TRP degradation in rigid media.

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- [2] C.H.Nicholls & M.T.Pailthorpe, J. Text Inst., 67 (1976), 397.
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TRIPLET PRODUCTS FROM GAMMA-IRRADIATED AQUEOUS NITROBENZENE SOLUTION

bv

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Industrial Technology Program, ANSTO, Menai, AUSTRALIA

ABSTRACT

This work shows that hitherto-unknown long-lived radical products are produced when aerated aqueous solutions of nitrobenzene are irradiated by Co60 gamma rays. The products have been separated and characterised.

The first radical product is a brown black amorphous solid which is slightly soluble in water, alcohol and acetone but not in acetonitrile or carbon tetrachloride. The ESR spectrum of this solid showed three pairs of shoulders on both sides of a centre line g=2.001 at H=3390G and the appearance of M=2 at 1600G, which clearly proves that it is a triplet. There is an intermolecular interaction between the unpaired electrons of two radical species a short distance apart forming associated singlet dimer and triplet dimer without making a new covalent bond (Kosower).

Thin Layer Chromatography and the Infra Red spectrum showed the species was ortho-nitrohydroxycyclohexadienyl radical.

Two other long-lived radical species were found during the course of this work. The method of preparation will be presented. One is a triplet. These have not been characterised.

Further work is still in progress and will be reported at the meeting.

References

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A REVIEW OF THE 'COLD NUCLEAR FUSION' PHENOMENON

bу

T.I. Quickenden

Department of Physical and Inorganic Chemistry, The University of Western Australia, Nedlands, W.A., 6009.

Abstract

The ability of palladium to store large quantities of hydrogen or deuterium and its well known catalytic properties have attracted considerable attention to palladium chemistry. However, the claim of Fleischmann, Pons and Hawkins (1) in 1989 that electrolysis of heavy water at palladium cathodes can cause fusion of deuterium atoms has created a period of unprecedented interest in palladium electrochemistry.

The history of the claims relating to electrochemically induced cold nuclear fusion will be reviewed and the current state of the field discussed.

References

(1) M. Fleischmann, B.S. Pons and M. Hawkins, <u>J. Electroanal. Chem.</u>, <u>261</u>, 301-308 (1989).

APPLICATIONS OF ELECTRON SPIN RESONANCE IN RADIATION CHEMISTRY AND RADIATION DOSIMETRY - PROSPECTS, PROBLEMS AND OPPORTUNITIES

by

John F. Boas

Australian Radiation Laboratory, Lower Plenty Road, Yallambie, Victoria, 3085

Abstract

Electron spin resonance (ESR) has the advantage that it may be used to identify and follow changes which occur on an atomic scale in materials as a result of radiation exposure. From a detailed analysis one can determine the nature and concentration of the radiation induced species and, in some cases, the nature of the sites at which these species are found. A major advantage is that ESR measurements are "non-destructive", i.e. the information is not destroyed by the measurement process.

Despite its apparent simplicity, ESR has several difficulties when used as an analytic/dosimetric technique, for example

- (i) rather more radiation induced species may be required to obtain ESR detectable effects than are required for other techniques, e.g. thermoluminescence
- (ii) quantitative ESR measurements to better than 5% are difficult
- (iii) the radiation chemistry needs to be known before the system is used as a radiation dosimeter.

This paper will discuss the application of ESR to several areas of present and possible future interest in radiation chemistry and radiation dosimetry. These include fundamental studies of solid-state materials, food irradiation, high dose dosimetry (e.g. using alanine) and accident dosimetry.



GENERAL INFORMATION

VENUE

The Conference will be held in the AINSE Theatre (Institute Building) see map page 2 from Monday 5th - Wednesday 7th November, 1990.

PAPERS

Timing

Green light shows for presentation of paper, Warning lights show when 5 & 2 minutes are remaining, Red light shows when presentation time has expired, Discussion time of 5 minutes is then allowed by the Chairman.

Slides

Authors using 35 mm slides in conjunction with their talk are requested to place their slides in the projector magazine during the break preceding the session in which the paper is scheduled.

Poster Session

The Poster Session will be held in the AINSE Council & Conference Rooms at the scheduled time. Posters should be set up during the afternoon tea break before the Poster Session commences and taken down on Wednesday afternoon. Posters should be prepared before arrival at the Conference in accordance with the guidelines previously provided.

Authors are expected to be in attendance by their posters throughout the poster session.

Materials for setting up posters are available from any member of the AINSE staff.

ACCOMMODATION

For out of Sydney participants whose nominations have been previously accepted, accommodation has been arranged in accordance with advised requirements, at Stevens Hall, Lucas Heights (adjacent to the Institute Building, outside the Main Gate) - see map p2 or at the Metro Motor Inc, The Kingsway Miranda (Cnr Jackson Avenue) The Institute will make payment directly to the management for room only charges at Stevens Hall or the Metro Motor Inn. Participants should make personal arrangements to pay cash for breakfast charges. Participants are requested to vacate rooms by 10.00 a.m.on day of departure, and to leave their luggage in the room marked 'luggage' adjacent to the AINSE Theatre Foyer. Room keys to be left in the Reception Office.

MEALS

Breakfast

For Stevens Hall residents, breakfast is served in the ANSTO Canteen from 7.30 a.m.

For Metro Motor Inn residents, breakfast time to be

advised.

Participants should make arrangements to pay cash for breakfast charges at Lucas Heights and at the Metro Motor Inn.

Lunches

Conference Lunch - Monday 5th November, 1990
Lunch for all participants will be held in the Stevens
Hall Dining Room during the scheduled lunch period (ref.
programme).Cost included in Conference Functions payment
(ref. Conference Announcement)

Lunches - Tuesday 6th and Wednesday 7th November, 1990 Lunches may be purchased from the ANSTO Canteen.

Evening

Meals

Conference Dinner - Monday 5th November, 1990

6.45 - 7.00pm Sutherland Trade Union Club

Southern Cross Lounge 57 Manchester Road GYMEA (Cnr Kingsway)

Address: Prof. F.P.Larkins

University of Tasmania

BBQ: Tuesday 6th November, 1990

<u>Note:</u> No other meal service will be available at Lucas Heights on these evenings.

If required, an evening meal can be provided on Sunday evening in Stevens Hall. It will be necessary however, to book this meal with AINSE at least one week before.

TRANSPORT

Transport from Sydney Airport - Monday 5th November 1990

An ANSTO bus will leave the Australian Airlines Terminal (Sydney Airport) for Lucas Heights at 9.25 a.m. Kindly give your name to the driver when entering the bus. If any difficulty is experienced in locating the bus, the Australian Airlines Commonwealth Car Desk will advise details of its precise location.

Request to Participants Arriving on ANSTO Bus from Airport

As time will be limited, participants are asked to proceed directly to the AINSE Theatre and not to Stevens Hall rooms. Luggage may be left in a room adjoining the Theatre Foyer marked 'luggage'. Keys may be picked up from Stevens Hall Reception at any time turing the day.

Transport from Sydney Airport (excluding Special Arrangements for Wednesday, 12th November, 1988)

Taxis are available from the airport to:-

Lucas Heights,

Sydenham Railway Station - then train to Sutherland Station, Sutherland Railway Station - then bus to Lucas Heights, or taxi (ref. bus timetable below)

Note: Bookings must be made for all transport listed below - through AINSE, as transport is only provided if demand exists.

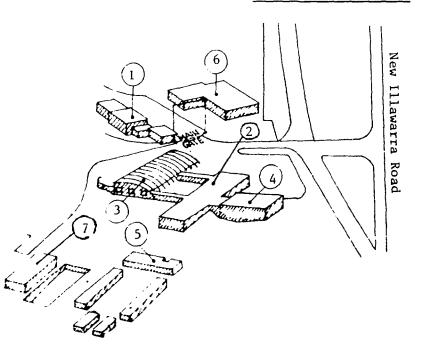
Monday - Friday

Tionay III	uay
Depart Lucas Heights for Sutherland	Depart Sutherland for Lucas Heights
6.15 a.m. 7.35 a.m. 8.30 a.m. 9.35 a.m. 10.35 a.m. 11.30 a.m. 12.30 p.m. 1.00 p.m. 2.15 p.m. 3.35 p.m. 4.50 p.m. 6.00 p.m. 7.30 p.m.	6.50 a.m. 7.55 a.m. 8.15 a.m. 9.05 a.m. 10.05 a.m 11.10 a.m. 12.00 p.m. 1.10 p.m. 1.30 p.m. 2.45 p.m.

Buses from Lucas Heights leave from outside ANSTO Main Gate

Buses from Sutherland Leave from outside Post Office, Flora Street.

LUCAS HEIGHTS N.S.W.



- 1. Main Gate
- 2. AINSE Euilding
- 3. Canteen
- 4. AINSE Theatre
- 5. Stevens Hall
- 6. Reception
- 7. Amenities Centre

TRANSPORT

Transport from Metro Motor Inn to Lucas Heights.

Please wait outside the Motel for pick-up at 8.20 a.m. It would be appreciated if participants with their own transport could drive to Lucas Heights and assist by transporting others if possible.

Transport from Lucas Heights to the Metro Motor Inn

Some buses leaving Lucas Heights will transport participants to the Metro Motor Inn, if required. It is necessary, however, to book for these services - through AINSE, as transport is only provided if demand exists.

Transport from Lucas Heights to Sydney Airport - Wednesday 7th November, 1990

Transport will be arranged to take participants to Sydney Airport after the Conference concludes. Please place your name on the list provided, on the noticeboard outside the Theatre, if you require this service.

Participants leaving Stevens Hall - Wednesday, 7th November, 1990
Participants are requested to vacate their rooms by 10.00 a.m. Luggage may be left in the room marked 'luggage' adjacent to the AINSE Theatre Foyer. Room keys may be left in the Stevens Hall Reception Office.

TELEPHONE MESSAGES

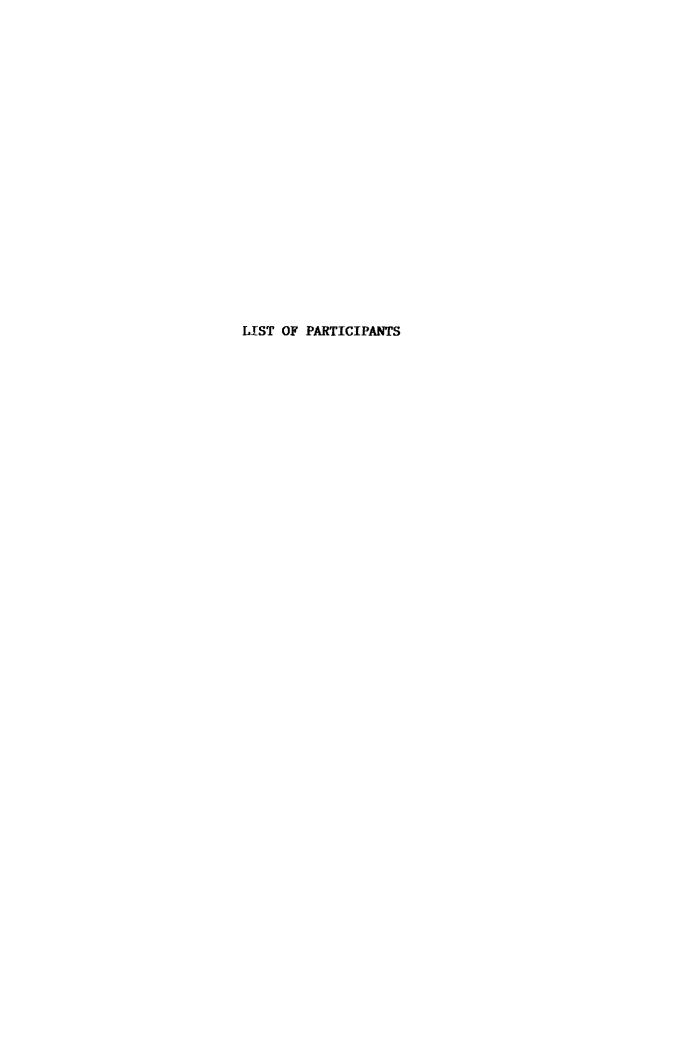
Telephone messages will be taken for conference participants on:-

543-3411 543-3436 543-3111 (AINSE) (Switchboard)

<u>All enquiries</u> concerning the Conference arrangements should be directed to:-

Ms. Joan Watson, Conference Secretary, A.I.N.S.E., Private Mail Bag 1, MENAI NSW 2234

Phone: 543-3411 or 543-3436



LIST OF PARTICIPANTS

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VISITORS FROM OVERSEAS	
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Dr. A.J.Swallow	2R
Patterson Research Labs.Manchester, U.K. Dr. R. Clough	21R
Sandia National Labs. New Mexico, U.S.A.	21 K
Professor V. Gromov	35R
Institute Physical Chemistry, Moscow, U.S.S.R.	
Professor Seuchi Tagawa	25R
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Science and Technology, JAPAN	מכר
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Ms. M.Turanek	18,20

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