8th "Tihany" Symposium

on Radiation Chemistry

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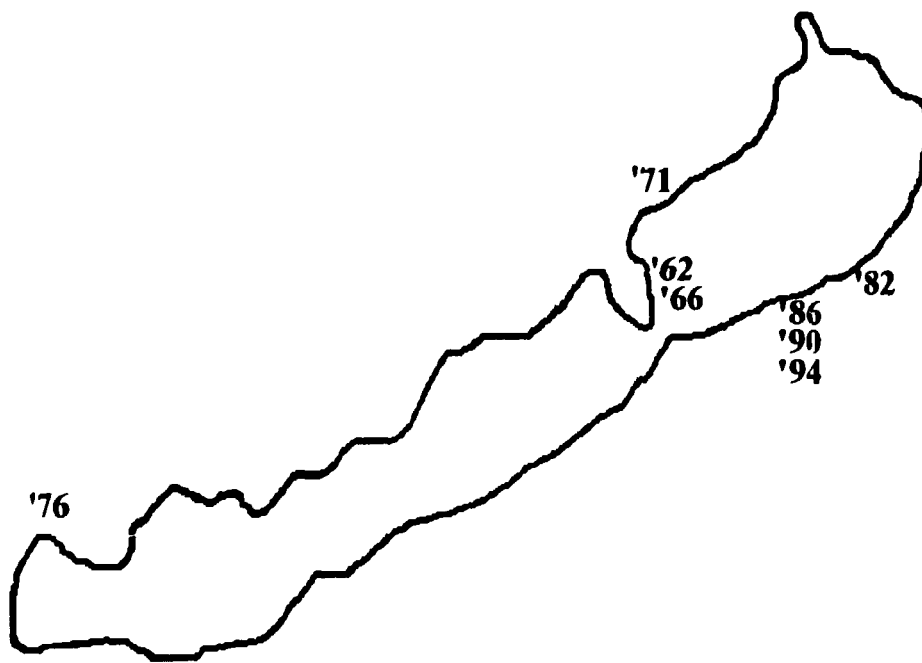
Organized by the

Hungarian Chemical Society, and

Institute of Isotopes of the Hungarian Academy of Sciences,

in co-operation with the

International Atomic Energy Agency,

PHARE ACCORD,

Hungarian Academy of Sciences, and

Hungarian National Committee for Technological Development

Lectori salutem!

The first international conference on radiation chemistry in Hungary was organized in 1962 in Tihany, on the northern shore of the Lake Balaton. The 86 participants came from 9 countries and from the International Atomic Energy Agency.

The topics were research and development in radiation chemistry and technology, without any further limitations. We believed and believe since that a meeting where basic problems of radiation research can be discussed along with applications, even with industrial questions and, in spite of all this, attendance is limited and ample time is given to informal exchange of views, may be regarded as an asset even if the calendar of radiation chemistry meetings is heavily packed.

The success of the Symposium can be attributed not only or not mainly to the papers given but rather to the possibilities for the above mentioned informal discussions of scientists arriving from both western and eastern countries, utilizing the geographical and partly political situation of Hungary.

Falling the demand the second "Tihany" Symposium was organized in 1966 followed by the further ones in every 4-6 years. Due to the increasing number of the participants from 1971 the symposia were not organized in Tihany any more but in all cases at the shore of the Lake Balaton (1971: Balatonfüred, 1976: Keszthely, 1982: Siófok). In 1986 and 1990 our Symposium were located at Balatonszéplak, i. e. at the same spot where the 8th one in the series is going now to be organized.
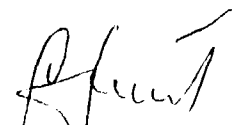
In the last deca ʿe of our century the "determining role" of the Tihany Symposia to be a bridge between East and West is - fortunately - not longer a point of view. At the same time, however, to strengthening connections with scientists of development countries.

When we think about the previous symposia it is my sorrowful duty to remember two key person of earlier "Tihany" Symposia: Professor Malcolm Dole from the United States and Géza Schay from Hungary who are no longer with us.

At the 8th "Tihany" Symposium more then 100 scientists participate from 23 countries from all region of the world. After the plenar opening we will have 14 oral sessions to present the 68 lectures (generally with 5 minutes discussions) and a poster session for 19 written texts.

As by the last meeting, an upswing of lectures on radiation biology and, partly, on photochemistry can be seen also now.

And last but not least in the spirit of the previous meetings also this Symposium is going to give an opportunity to free exchange of experiences and opinions

Gábor Földiák

General informations

Registration will take place at the Symposium site on Saturday, September 3 from 4.00 p.m. to 10.00 p.m. and on Sunday, September 4 from 8.00 a.m. to 1.00 p.m.. A.. information service will be at your disposal in the lobby of the hotel during the whole Sympos:.um.

Meals will be served at the restaurant of the hotel.

Coffee ard soft drinks will be available in the buffet of the hotel in each break.

The **swimming pool** will be at your disposal from 6.00 am to 9.00 pm. free of charge.

The **half-day excursion** for all participants will take place on Tuesday, September 6, by buses starting in front of Hotel Ezüstpart. Participants will be taken to the northern shore of the Lake Balaton and the tour will include sight-seeing and cultural programme. The excursion will be followed by the conference dinner in a country pub.

A **full-day Ladies' programme** will be organised on Wednesday, September 7 to Veszprém (sight-seeing), Herend (china factory), Zirc (monastery).

Scientific programme

Saturday, September 3

16.00 - 22.00 Registration

19.00 Welcome

Sunday, September 4

9.00 Opening

    1. **S. Machi**: New Trends of Radiation Processing Applications.

10.00 - 10.20 Break

10.20 - 12.20 Session 1 *Chairman: V. Markovic*

    2. **P. Mittal**: Radiation Chemistry of Fullerenes: Pulse Radiolysis and Steady State Studies

    3. **D. Trifunac**, E. Piocos, D. Werst: Radical Cations in Zeolites

    4. **S. Tagawa:** Application of Pulse Radiolysis to Polymers for Microelectronics

    5. **I. Kaetsu**: Biomedical Materials by Radiation Techniques

    6. **J. McKeown**: Waste Treatment Revisited - Curiosity or Opportunity?

    7. **N. Sheik**: Application of Radiation Chemistry for Image Restoration of the Ancient Iranian Potteries

13.00 - 14.00 Lunch

14.00 - 16.00 Session 2 *Chairman: A. Charlesby*

    8. **J. Mayer**, M. Szadkowska-Nicze, J. Kroh: Charge Transfer Processes in Polyethylene

    9. **N. Betz**, E. Petersohn, A. Le Moel: Electron Spin Resonance Study of Swift Heavy Ion Irradiated Fluoropolymers

    10. **H. Mirzadeh** , A. A. Katbab, M. T. Khorasani, R. P. Burford: Laser Induced Surface Grafting of Acrylamide `nto Ethylene-Propylene Rubber-III, Effect of Pulse Repetition Rate on Surface Morphology

    11. **T. Czvikovszky**: Electron-Beam Processing of Wood Fiber Reinforced Polypropylene

    12. **D. Lebedev**: Radiation and Photochemical Chlorination of Paraffins in Liquid Phase

    13. K. Friese, B. Hösselbarth, **J. Reinhardt**, R. Newe: The Radiation-Induced Solution Chlorination of PVC

16.00 - 16.20 Break

14. C. Hueber, **C. Chuaqui**, S. Dickinson, D. Jacquemain: Radioiodine Chemistry in Light Water Reactor in Severe Accident

15. **I. Dvornik**, S. Miljanic, Z. Deanovic: The Probability of Lethal Radiation Effects as Related to Nuclear Accident Dosimetry Data

16. **Y. Katsumura**, G. R. Sunaryo, D. Hiroishi, K. Ishigure: Radiolysis of Water at Elevated Temperatures with Gamma-Rays and Fast Neutrons

17. **M. Domae**, Y. Katsumura, K. Ishigure, V. Byakov: The Model of Initial Intratrack Chemical Processes of Water Radiolysis

Monday, September 5

9.00 - 11.00   Session 4   *Chairman: J. Dobó*

18.   **J. L. Garnett**: Curing review

19.   **P. Hedvig**: Mechanical and Dielectric Relaxation of Radiation Crosslinked Polymers

20.   **V. I. Feldman**:Fundamental Aspects of Selectivity of the Radiation-Induced Processes in Hydrocarbons and Related Polymers

21.   **E. Takács**, L. Wojnárovits: Pulse Radiolysis Studies on Polymerization Kinetics

22.   **Y. Berlin**: Randomly Affected Kinetics Applied to Reactions of Chemically Active Species in Irradiated Condensed Media

11.00 - 11.20   Break

11.20 - 12.40   Session 5   *Chairman: S. Tagawa*

23.   **R. Schaudy**, J. Wendrinsky, R. J. Beer, J. Eberhardsteiner: Irradiation of Polymers for Photoelastic Investigations

24.   **A. A. El Miligy**, E. A. Hegazy, H. Kamal: Physico-Chemical Properties of Membranes Obtained by Radiation Grafting Onto FEP Films

25.   **El-Sayed A. Hegazy**, H. Kamal: Ion - Containing Membranes Obtained by Radiation Grafting of Individual and Binary Monomers Onto Polymeric Substrates

26.   **S. Aliaoui**: Immobilization of Antibodies on Polymers Grafted by Irradiation

13 00 - 14.00   Lunch

14.00 - 16.00   Session 6   *Chairman: I. Dvornik*

27.   **Z. P. Zagórski**: Emission Spectra and Decay Kinetics of Pulse Irradiated Polycrystalline Tryptophans

28.   **I. György**, K. Gonter, A. Kovács: Decomposition of Halogen Containing and Phenolic Pesticides: Pulse Radiolysis Investigations

29.   **K. Bobrowski**, C. Schöneich: Decarboxylation Mechanism of N-Terminal Glutamyl Moiety in Methionine Containing Peptides

30.   **M. I. Cshtrakh**, E. A. Kopelyan, V. A. Semionkin: Mössbauer and Positron Annihilation Study of Oxyhemoglobin Exposed to Gamma-Rays and Electrons

31.   **H. Durchschlag**, B. Feser, C. Fochler, S. Hausmann, E. Swoboda, T. Seroneit, P. Zipper: Effects of X- and UV-Irradiation on Proteins. I. Probing the Stability of Proteins by Different Techniques

32. **H. Durchschlag**, C. Fochler, M. Swientek, A. Winklmair, C. Wlcek, P. Zipper: Effects of X- and UV-Irradiation on Proteins. II. The Modification of Irradiation of the Enzyme Lysozyme

33. C. Fochlei, **H. Durchschlag**: Effects of X- and UV-Irradiation on Proteins. III. The Interaction of Radiation with Eye Lens Proteins

16.00 - 16.20 Break

16.20 - 18.00 Session 7   *Chairman: A. Miller*

34. Lj. Josimovic, **M. Radojcic**, B. H. Milosavljevic: Radiation-Induced Effects in Protein-Rich Organic Matter the Thin Fraction of Egg White

35. M. Szczepanik, **S. Ignatowicz**: Identification of Irradiated Insects: Change in the Midgut of the Confused Flour Beetle, Tribolium Confusum Duv., Induced by Gamma Radiation

36. **S. Farag**, G. Schulzki, K. Bögl, G. Schreiber: Detection of Irradiated Fruits by Gas-Chromatographic Methods

37. O. A. Emam, **S. Farag**, A. I. Hammad: Comparative Studies Between Fumigation and Irradiation of Semi-Dry Date Fruits

38. **L. G. Gazsó**, A. M. Dám, M. Rétlaki: Determination of Radiation Sterilization Dose of Health Care Products Based on ISO Standards

39. **A. M. Dám**, L. G. Gazsó, S. Kaewpila, I. Maschek: Radiation Treatment of Pharmaceuticals

Tuesday, September 6

9.00 - 10.00   Session 8   *Chairman: J. Mayer*

40.   **J. L. Garnett**: The Role of Partitioning of Reagents in Grafting and Curing Reactions Initiated by Ionising Radiation and UV

41.   **I. Czajlik**, P. Hedvig, A. Ille. , J. Dobó: Calorimetric Study of Cationic Photopolymerization

42.   **R. Vahrik**, A. Ille, A. Vig, I. Czajlik: Thermomechanical Investigations of UV Cured Epoxy Coatings

10.00 - 11.00   Session 9 (Poster Session)   Chairman: W. L. McLaughlin

P1.   **V. Zubarev**, O. Brede: Radiation-Chemical Peculiarities of Spin Trapping

P2.   **L. Goebel**, O. Brede, T. Zimmermann: Photochroism of a New Spiroindoline Compound

P3.   **V. I. Feldman**, F. F. Sukhov, N. A. Slovokhotova, V. P. Bazov: Radiation-Induced Degradation of Alkane Molecules in Low-Temperature Matrices

P4.   **B. Vekic**, A. -M. Dogic, D. Razem: Nonthermal Electron Scavenging in n-Hexane

P5.   **M. Jonsson**, J. Lind, G. Merényi, T. E. Eriksen: Redox Chemistry of Substituted Anilines

P6.   O. Brede, R. Hermann, **H. Orthner**: Charge Transfer to a Semi-Esterified Bifunctional Phenol

P7.   **Y. Keheyan**, R. Bassanelli: Ion-Molecule Reactions Studied by Nuclear Decay Technique. Tritiated Naphthylium Ions

P8.   **B. Mihaljevic**, D. Razem: Free Radical Chain Oxidation of Fe^{2+} by Hydroperoxides

P9.   **G. Chlebosz**, J. Kalecinski: Stability of Trapped Electrons in Thermally Modified Alcohol-Alcohol and Alcohol-Water Glasses

P10. **B. K. Razem**, D. Razem: The Modelling of Radiation-Induced Hydroperoxidation in Solid Systems

P11. **H. Sprinz**, O. Brede: Lipid Oxidation in Bilayer Liposomes Induced by Radicals from the Surrounding Water Phases

P12. **E. Kalecinska**, J. Kalecinski: Reactivity of Imidazoles in Pulse and Gamma-Irradiated Liquid and Frozen Systems

P13. **W. Knolle**, R. Mehnert: On the Mechanism of the Electron-Initiated Curing of Acrylates

P14. **G. Burlinska**, J. Bojarski: ESR Studies of Irradiated Polypropylene and ITS Copolymers

P15.	**G. Burlinska**, D. Pogocki, K. Bobrowski: ESR Study of Radiation Induced Radicals in Polycrystalline Methionine and ITS Homopeptides
P16.	**O. I. Shpotyuk**, A. P. Kovalsky: New Radiation Dosimetric Systems Based on Amorphous Chalcogenide Semiconductors
P17.	**I. Pucic**, F. Ranogajec: Influence of Electrical Field and Dose Rate on Radiation Curing of Unsaturated Polyester Resins
P18.	**A. P. Shvedchikov**, E. V. Belousova, A. V. Polyakova, A. Z. Ponizovsky: Oxidation of Ammonia in Moist Air by Use of Pulse Corona Discharge Technique
P19.	**E. Rémi**, O. Horváth, A. Víg, A. Rockenbauer, L. Korecz, I Rusznák: Studies on Photofading and Stable Free Radical Formation in Reactive Dyed Cellulosic Systems Under Their Exposure to Light

12.00 - 13.00 Lunch

13.00 - 23.00 Excursion, conference dinner

Wednesday, September 7

9.00 - 11.00   Session 10   *Chairman: A. D. Trifunac*

43.   T. Bandyopadhyay, G. Nagy, **R. Schiller**: Energy Distribution of Slow Electrons in a Hard-Sphere Liquid

44.   **Sz. Vass**, B. Molnár, Cs. Szeles, K. Süvegh, A. Vértes: Positron Annihilation in Liquid Normal Hydrocarbons

45.   **L. Wojnárovits**, J. A. LaVerne: Radical Reactions in the Radiolysis of Cyclopentane

46.   **J. A. LaVerne**, L. Wojnárovits: Heavy Ion Radiolysis of Cyclooctane

47.   **G. Földiák**, M. Roder, L. Wojnárovits: Influence of Linear Energy Transfer on Reactions of Cycloalkyl Radicals

48.   **P. G. Di Marco**, N. Camaioni, V. Fattori, G. Giro, J. Kalinowski: Electroluminescence in Organic Solids

11.00 - 11.20   Break

11.20 - 13.00   Session 11   *Chairman: P. Sharpe*

49.   **A. Miller**: Uncertainty of Dose Measurements in Radiation Processing

50.   A. Kovács, L. Wojnárovits, S. E. Eid, **W. L. McLaughlin**, A. Miller: Radiation Chemical Reactions of Triphenyl-Tetrazolium Chloride in Liquid and Solid State

51.   K. K. Mehta, **I. Janovsky**: Measurements of Electron Depth-Dose Distribution in Thick Plastics and Effects of Accumulated Charge

52.   **R. Yefsah**: Development of Silver Dichromate on Dosimetry

53.   V. G. Shpak, **M. I. Yalandin**, S. A. Shunailov: Desktop Repetitive Sources of Powerful Electron Beams, X-Ray and Microwaves for LAB Investigations on Radiation Chemistry, Physics and Biology

13.00 - 14.00   Lunch

14.00 - 15.40   Session 12   *Chairman: H. Yoshida*

54.   Y. Chen, **R. H. Schuler**: Oxidation of Benzoquinone by Radiolytically Produced OH Radicals

55.   Qun Sun, G. N. R. Tripathi, R. H. Schuler, **D. A. Armstrong**: Redox Chemistry of Some Phenyl Thiyl Radicals

56.   **K. Kishore**, G. R. Dey, P. N. Moorthy: Pulse Radiolysis of 2, 5-dimercapto Thiadiazole

57.   **K. Sehested**, J. Holzman: A Pulseradiolysis Study of the OH Radical Induced Autoxidation of Methanesulphinic Acid

58.   **Á. Bíró**, L. Wojnárovits: Reaction of Diethyl Maleate and Diethyl Fumarate with Hydrated Electrons and Hydroxyl Radicals

15.40 - 16.00   Break

59. J. Kumagai, T. Ichikawa, **H. Yoshida**: Radical Ions of Oligosilane and Polysilane

60. **T. Nishida**: Gamma-Ray Induced Crystallization of Oxide Glass, Nitrate Glass and Egg-White Glass

61. **D. D. Lebedev**, I. V. Dobrov, S. E. Pavlov: Radiation-Chemical Synthesis of Monochloroexchanged Methylchlorosilanes

62. **J. Kalecinski**: Scavenging of Electrons and Radicals in Frozen Chloride-Alcohol Glasses

63. **H. Bahadur**: Radiation Effects on Aluminium and Hydrogen Defects in Natural Quartz

64. **H. Bahadur**: Radiation Effects on Hydroxyl Defects in Ge-Doped Quartz

Thursday, September 8

9.00 - 10.00 Session 14   *Chairman: K. Sehested*

65. **G. Merényi, J. Lind:** Some Aspects of Bromine Atom Chemistry

66. **R. Zhao, J. Lind, G. Merényi, T. E. Eriksen:** On the Kinetics of One Electron Oxidation of Thiols and Hydrogen Abstraction by Thiyl Radicals from -Amino C-H Bonds

67. **D. B. Naik, W. Schnabel:** Studies on Laser-Induced Photoionization of Tris-2, 2'-Bipyridyl Ru(II) Complexes in Polyelectrolyte Solutions

10.00 - 10.20 Break

10.20 - 11.00

68. **A. Charlesby:** Radiation, its Nature, Interactions and Potential Applications

Closing

12.00   Lunch

NEW TRENDS OF RADIATION PROCESSING APPLICATIONS

S. Machi

International Atomic Energy Agency, Vienna, Austria

Major fields of radiation processing applications are: polymeric materials, food processing, sterilization of medical products, and environmental conservation. These applications are growing and new developments are being studied in both developed and developing countries. There are about 200 Co-60 gamma irradiation facilities and 700 electron beam accelerators mainly for commercial purposes throughout the world.

Radiation cross-linking and grafting techniques of polymeric materials have been providing many unique products including heat and chemical resistant insulation materials, heat shrinkable sheets and tubes, foamed plastics, curing of coatings, battery separators, and bio materials.

Currently 27 countries, half of which are developing countries, are using radiation technology for treatment of food for commercial purpose to decrease post-harvest food losses, to avoid food-borne diseases and enhance international food trade. Public acceptance of irradiated food has been improved.

Removing SO_2 and NO_x by electron beams is a good example of radiation processing applications for environmental protection. In Japan, USA, Germany, and Poland pilot scale plants, using electron beam accelerators, have been successfully operated to simultaneously remove 80% NO_x and 95% SO_2. An industrial demonstration plant for this technology is planned under an IAEA TC project in Poland.

Extensive studies have been devoted to the development of bio-medical materials using radiation processing to prepare bio-compatible materials and controlled release of drugs. New wound dressings have been successfully developed in Poland for commercial clinical use.

Abstract was not submitted

Radical Cations in Zeolites

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Argonne National Laboratory
Argonne, IL 60439

Zeolites are convenient and relatively rigid matrices allowing radiolytic production and stabilization of a wide variety of hydrocarbon radical cations. The study of several radical cations illustrated the possibility of turning the interaction between the matrix and the ion, allowing observation of many diverse and otherwise not observable radical cation transformations, which do not occur or are photodriven in other matrices. Many transformations occur in the low temperature zeolite matrix. A remarkable stabilization of otherwise higher electronic levels of ions and/or a significant lowering of reaction barriers must be occurring.

Abstract was not submitted

Biomedical Materials by Radiation Techniques

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Radiation polymerization of supercooled monomers was studied systematically and applied to the immobilization and controlled release of biofunctional materials. The degree of firmness and looseness of immobilization can be controllable widely. This technique has beenvariously modified and applied extensively to bioreactors, biosensors, artificial organs, diagnostic systems and drug delivery systems. Especially, the application to drug delivery systems has been carried out successfully for local chemotherapy and hormone therapy.

Recently, the target of our research interest has turned to the function of brain-nervous system from the cancer therapies. The reasons are : (1) Drug delivery system is tending to a new generation, to have an intelligence function. Thus, a combination of sensor and delivery system has become the important subject for this purpose. The most ideal model of intelligent system is the neuron-synapse system and the neural network. (2)As well known,smell substances cause remarkable physiological and psychological effects on the brain. Therefore, the controlled release technique of smells can contribute to the clarification research of brain-mental functions with the intelligent smell delivery system. (3) Recently, various non-invasive measurements for mental and psychological actions have been developed. Those means can be used effectively in combination of intelligent smell delivery system and drug delivery system for neuro-drug and neuro-transmitter.

The scope and strategy for brain research with biomedical means and materials would be reported in the symposium.

WASTE TREATMENT REVISITED - Curiosity or Opportunity?

J. McKeown

AECL Accelerators
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The seventies and early eighties provided high expectations [1,2] for the adoption of electron treatment of waste. Despite unassailable evidence of assured disinfection, more than a decade has passed and work continues to be concentrated in the laboratory. The potential for displacement of chemical oxidants by radiation on scientific grounds, remains insufficient to trigger the building of municipal systems. Reasons for the lack of commitment are complex. An indication may be found from AECL's experience with a recent proposal on a Sludge Management Plan submitted to the City of Edmonton, Canada. A study of this case provides economic assessments of competing technologies and could provide incentives for renewed research at the basic radiation chemistry level.

1.   Trump J.G., "Disinfection of Municipal Wastewaters and Sludges by Ionizing Radiation", Proc. Conference on Disinfection of Wastewater Effluents and Sludges, pp. 125-151, University of Miami, NTIS No. PB 87-206223/AS (1984).

2.   McKeown J., "Electron Accelerators - A New Approach", Radiat. Phys. Chem. Vol. 22, No. 3-5, pp. 419-430 (1983).

APPLICATION OF RADIATION CHEMISTRY FOR IMAGE RESTORATION OF THE ANCIENT IRANIAN POTTERIES

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One of the problems with ancient colored potteries, which have been obtained by excavation, is disappearance of their superficially figures. In this cases, archaeologists wet the surface of these pieces with water then the underlying figures temporarily become visible with their original appearance.
This disappearance of the figures is formed after excavation due to the movement of the artifact from its original ambient conditions to a new environment.
This results in the disruption of the equilibrium conditions of the artifact.
It has been reported in previous investigation that this disappearance is due to partial or total loss of the water of hydration of the inorganic dyes or pigments used in the preparation of these objects (Guven, 1983).
This interpretation does not appear to be entirely valid beacause in a majority of cases these dyes or pigments are metal oxides and so lack water of hydration. It is the author's considered opinion that this defect perhaps has more to do with the deterioration of the top glaze.
It is believed that a special chemical reaction, thermal shock, pressure or an impact may have led to the loss of transparency of the top glaze and thereby the underlying figures of glaze may have disappeared.
On the other hand polymeric materials with the aid of radiation processing provide a satisfactory solution to this problem. In this method by superficial application of some of the oligomers to the samples and subsequent irradiation with gamma-rays, complete polymerization of oligomers is achieved and a thin transparent polymeric layer is formed.
In the present work some of colored potteries belonging to the Elkhany period, excavated at Soltanieh, an old Iranian city, have been restored by this method.

CHARGE TRANSFER PROCESSES IN POLYETHYLENE

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Technical University, Łódź, Poland

Pulse radiolysis of pu,_ethylene (PE) containing aromatic compound (pyrene, Py; dimethyldiphenyl, DMD) generated corresponding radical ions. In the case of Py two well separated absorption bands were observed: at 450 nm and 500 nm attributed to Py radical cation (Py$\cdot^+$) and Py radical anion (Py$\cdot^-$) respectively. The maxima at 420 nm and 650 nm in absorption spectrum of pulse irradiated PE containing DMD represented DMD radical ions.

Analysis of the ion decay curves showed that the kinetic model with time-dependent rate constant satisfactorily described the experimental results. For both, Py and DMD radical ions corresponding Arrhenius plots were characterized by two linear parts which intersected in the Tg, glass transition temperature range 220-240 K, for PE. The activation energies, for decay of both kind of ions, calculated from two parts of Arrhenius plot were equal to ca. 79 kJmol^{-1} and ca. 2 kJmol^{-1} for T>Tg and T<Tg respectively.

The recombination of radical ions in PE produced solute excited states (singlet and triplet ones).

Pulse radiolysis of PE containing two solutes, Py and DMD, generated both kind of ions.

The charge transfer from DMD ions to Py was observed and analysed. Activation energy of this process was found to be similar to those obtained for ion-recombination in temperature range higher than Tg. The mechanism of primary and secondary events in pulse irradiated PE containing aromatic solutes will be presented.

Electron Spin Resonance Study of Swift Heavy Ion Irradiated Fluoropolymers

N. Betz, E. Petersohn, A. Le Moël

Commissariat à l'Energie Atomique, DSM/DRECAM/Service de Recherches sur les Surfaces et l'Irradiation de la Matière, 91191 Gif-sur-Yvette Cedex, France

Heavy ion irradiation of polymers induces deep modifications in the physico-chemical properties of polymers. Ions create on their wake through the solid a high density of excitations and ionisations which changes the polymer properties in a small cylindrical damage zone, the latent track. This leads to an anisotropic composite in opposite to traditional irradiations with electron or γ-ray.

In the last years, the effects of ion beams on poly(vinylidene fluoride) (PVDF) have been accurately investigated in our laboratory. Only a few studies have been reported on electron spin resonance measurements of PVDF in its α phase after swift heavy ion irradiation in the range of high irradiation doses, though the radical distribution which occurs by means of electron or γ-irradiations was well investigated.

We present here a study of swift heavy ion irradiated films of PVDF in its α phase and its bi-stretched ferroelectric β phase. Moreover we draw a parallel with the qualitative and quantitative information obtained on free radical species in ion irradiated copolymer films of vinylidene fluoride and trifluoro ethylene (P(VDF/TrFE)).

We have compared the structure and the concentration of radicals in the polymers after irradiation with swift heavy ions (oxygen, tin,...) in a dose range up to 600 kGy. The spectrum of irradiated α PVDF is reasonably attributed to radicals of alkyl and peroxy type due to chain scission and further radical reactions with oxygen. In irradiated β PVDF, the structures of the radicals are more resolved, this behaviour can be attributed to the bi-stretching of β PVDF which leads to a more ordered structure in the polymer. Despite the fact that the copolymer P(VDF/TrFE) crystallises in the same orthorombic structure as the β PVDF, the spectra exhibit only the asymmetric peroxy radical. The evolution of the calculated radical concentration per ion with absorbed dose or fluence shows differences depending on the type of polymer. The exponential decreasing indicates an increased possibility of radical recombination may be overlapping of latent ion tracks for high irradiation doses.

We also studied the effect of temperature on radical stability. Additional radical structures appear in the temperature range of 298 K to 453 K besides the weakening of radical concentration. The kind of structure observed was never reported in ESR studies of irradiated polymers. It is characteristic of swift heavy ion irradiation. This effect is explained by the variation in the crystalline structure of the irradiated polymers leading to differences in radiation inertness and resistance to heat. A study of temperature annealing at 333 K confirms the results and interpretations by differences in the structure of the polymers.

LASER INDUCED SURFACE GRAFTING OF ACRYLAMIDE ONTO ETHYLENE-PROPYLENE RUBBER-III, EFFECT OF PULSE REPETITION RATE ON SURFACE MORPHOLOGY

H. Mirzadeha, A. A. Katbabb, M. T. Khorasania, R. P. Burfordc

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b, Department of Polymer Engineering, Amirkabir University, Tehran, Iran
c, Department of Polymer Science University of New South Wales, Sydney, Australia

The status of the polymer surface is important for many properties and applications, including chemical resistivity, adhesion, wettability, permeability and bio-compatibility. Therefore, surface modification of a polymer with optimum bulk properties is an efficient way to make it suitable for the desired application.

To improve bio-compatibility, attempts have been made to provide hydrophilic sites onto the surface of ethylene-propylene rubber (EPR) by grafting acrylamide (AAm) as hydrophilic monomer onto the surface of hydrophobic EPR, using CO_2-pulsed laser as excitation source. This surface specific technique should allow substrate bulk properties to be retained.

Scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDXA) and attenuated total reflectance infrared (ATR-IR) spectroscopy performed on the modified samples revealed the formation of grafted poly(AAm) on the surface of EPR. The modified samples showed improved surface hydrophilicity. Surface morphology of the modified EPR can be controlled, by varying the lasing parameters such as repetition rate.

The morphology and property of the grafted samples by laser-initiated polymerization are highly dependent on the laser operating parameters. In this paper we focus on the critical role of laser pulsing frequency in the morphology of the grafted EPR samples. In general, as the interval between successive laser pulses is decreased, the overall graft yield is diminished and the hydrophilic/hydrophobic balance is also varied.

Tissue compatibility (in vivo) of the modified EPR has also been investigated. Better tissue compatibility was observed for the laser-modified samples compared with the unmodified controls.

Electron-Beam Processing of
Wood Fiber Reinforced Polypropylene

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High aspect ratio (L/D>100) cellulosic fibers can be used as efficient reinforcement for different thermoplastics.

A procedure has been developed for wood fiber reinforced thermoplastic composites, applying a relatively small amount of reactive additive that compatibilize the synthetic and natural polymer components. Electron Beam (EB) treatment is a productive method of creating active sites on both matrix polymer and fibrous reinforcement, bound together through reactive additive.

The EB-processed, wood fiber reinforced polypropylene composite has not only a high modulus of elasticity, but also significantly higher flexural and tensile strength and improved thermal tolerance over the conventional wood fiber - polypropylene blends. The relatively low melt viscosity of our wood fiber reinforced polypropylene makes it easily processed not only by extrusion but also by injection molding. In the procedure recycled raw materials (e.g. fibers from recycled paper pulp or byproducts of the woodworking industry) can be used and the product is a fully recyclable composite.

The original procedure elaborated in Hungary was further developed and tried out in pilot scale at Canada. EB treatment, extrusion and thermoforming of the extruded sheets has been performed and applied to produce internal automobil parts, with the cooperation of Atomic Energy of Canada Ltd. (AECL) Whiteshell Research Laboratories. Technical feasibility and improved product quality has been demonstrated. The justification of high upfront investment costs of the EB processing line remained in discussion.

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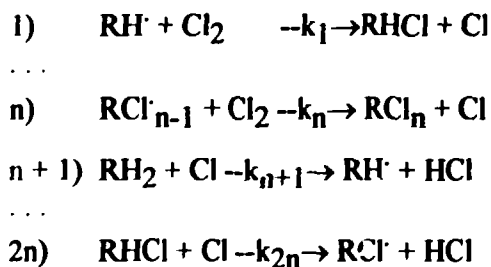   Hanser Publ., -Oxford Univ. Press, Münich-Vienna- New York, 1992.

RADIATION AND PHOTOCHEMICAL CHLORINATION OF PARAFFINES IN LIQUID PHASE

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By chlorination of the same paraffin under gamma-radiation and UV the following ratio is kept: $W_{pH}/W_{rad}=(W_{oph}/W_{orad})^{0.5}$. The reaction of chain propagation of n-stage process irrespective of the initiation method are given by following scheme:

1) $\quad RH^{\cdot} + Cl_2 \quad --k_1 \rightarrow RHCl + Cl$

. . .

n) $\quad RCl^{\cdot}_{n-1} + Cl_2 --k_n \rightarrow RCl_n + Cl$

n + 1) $\quad RH_2 + Cl --k_{n+1} \rightarrow RH^{\cdot} + HCl$

. . .

2n) $\quad RHCl + Cl --k_{2n} \rightarrow RCl^{\cdot} + HCl$

Having differentiated the current concentration by an initial component we have the equations which include $k_{n+1\ldots2n}$-constants only, determining the selectivity of chlorination. The constants of chain termination and $k_{1\ldots n}$ are not included in the differential equations.

In a liquid phase $k_{n+1\ldots2n}$ is 2.5-3 orders less than in gaseous phase, because in the liquid phase during the disintegration of the transfer state by the scheme:

$$C^{\delta+} -H^{\delta-} Cl \Leftrightarrow C \quad H^{\delta+} - Cl^{\delta-}$$

the probability of the reversible process increases. The cause is reorganization of surroundings, i. e. the change of geometry of the structure: molecule $\rightarrow$ radical and redistribution of the charge, but not the formation of complex or solvatation. The decrease of preexponent in a liquid phase as against a gaseous phase is the evidence of this. The calculation of A_o for C_2HCl_5 is equal to 4.2×10^6 and 4.5×10^9 l/Ms respectively. The elementary rate constants of the reaction $RH+Cl \rightarrow R^{\cdot} + HCl$, $RH=C_2HCl_5$ etc.:

C_2HCl_5 $(2.4+0.2) \times 10^4$ (20°) l/Ms;

$C_5H_{11}Cl$ $(1.5 +0.1) \times 10^5$ (24°) l/Ms;

$C_{14}H_{30}$ $(2.3+ 0.1) \times 10^5$ (20°) l/Ms

has been found from the experiment.

The radiation-induced solution chlorination of PVC

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For more than 50 years the solution chlorination of PVC has been an industrial process.
The result is a chlorinated PVC with chlorine content between 61 and 65 %. The high
solubility in the usual solvents makes the chlorinated PVC most suitable for laquers,
adhesives and fibres.

Of a great number of possible, but mostly toxic solvents, only tetrachloroethane was used
for the industrial production of chlorinated PVC. The chlorination of this solvent
produces hexachloroethane as an unwanted waste product.

For this reason, the solution chlorination of PVC in methylene chloride was studied.
Because of the low boiling point, the reaction between chlorine and PVC dissolved in
methylene chloride must be carried out under pressure.

The first experiments with thermal initiation were not so succesful, so the investigation of
the radiation-induced chlorination of PVC was started.

The apparatus for chlorination will be described, and in addition to this the main para-
meters of the reaction will be reported.

The results of many experiments show that during the reaction between chlorine and
PVC the solvent (methylene chloride) is chlorinated only in a small percentage to chloro-
form (9.5 %) and finally to tetrachloromethane (0.1 %).

Some details concerning the optimum reaction conditions and the influence of PVC-type
and solution concentration will be presented as well as the properties of the radiation-
induced chlorinated PVC in comparison with the conventionally produced CPVC.

It was found that the radiation-induced chlorinated PVC has the same structure as the
thermally chlorinated polymer, while the thermal stability and the speed of degradation of
the radiation products show the better data for application purposes.

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RADIOIODINE CHEMISTRY IN LIGHT WATER REACTOR IN SEVERE ACCIDENT

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In the event of a severe accident of a light water nuclear reactor, the core overheats and releases radioactive materials, including fission products. These materials are transported into the primary circuit, finally reaching the containment building, which is the last barrier to keep radioactivity under control.

Iodine radioisotopes, notably ^{131}I, are major components of the fission products released during the accident. This element can form volatile species that are a biological hazard during the first few days after the accident. As a consequence, iodine chemistry is one of the most important subjects of research in the chemical field of reactor safety.

We will present in this paper the main aspects of iodine chemistry in the containment building after a severe nuclear accident.

Aerosols containing caesium iodide, formed in the primary circuit, are transported into the sump of the containment building. Iodine is in the aqueous phase initially in the form of the iodide ion, I^-, which is transformed by γ-radiolysis (produced by fission products) into molecular iodine, I_2. This latter species participates in a disproportionation reaction via hypoiodous acid, HOI. I_2 can be also transferred to the atmosphere and absorbed by surfaces. Iodine is very reactive and can react with organic sources of the containment (i. e. painted surfaces) to form organic iodides, which are also volatile.

These phenomena are modelled in computer codes, which are validated by means of experimental programmes performed at different scales.

The probability of lethal radiation effects
as related to nuclear accident dosimetry data

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Nuclear accident dosimetry is the most important source of data for the early diagnosis and prognosis of acute radiation sickness (ARS). The problem of the relationship between expected acute radiation effects (probability of death or recovery, LD_{50}) and radiation dose (dose on the body surface measurable by personal dosimeters, depth dose distribution, dose to critical organs) is described for some typical radiation fields produced by catastrophic or accidental radiation events. For two different neutron plus gamma radiation fields the depth dose distributions were measured by "DL-M4" chemical personal dosimeters. The diagnostic value (advantages, limitations) of the maximum tissue-equivalent total neutron plus gamma dose directly measured by personal dosimeters on the body surface is analysed by applying the Gozembuk/Keirim-Markus model (1988, of our paper for The Seventh Tihany Symposium, pp. 549-55, refs. 8-14) of dose dependence of acute radiation effects.

Radioiysis of Water at Elevated Temperatures with γ-Rays and Fast Neutrons

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Determination of G-values of water decomposition products in neutral water produced by irradiation with γ-rays and fast neutrons at elevated temperatures up to 250°C was carried out by a combination of $NaNO_3$, acetone + methanol and $HClO_4$ + methanol solutions. From the measurement of the H_2 yields for these solutions, the G_{H2}, $G_{H2}+G_H$, and $G_{eaq}+G_{H2}+G_{OH}$, respectively, have been determined. From a mass balance relation, the value for water decomposition, G_{-H2O}, was calculated. The yields of H_2O_2, formaldehyde and ethyleneglycol produced as a function of dose in the $NaNO_3$ and $HClO_4$ + methanol solutions were chosen to derive the G_{OH} and G_{H2O2} from the simulation of the experimental results.

In the γ-radiolysis, the G-values obtained in the present experiment are in good agreement with recently reported ones except G_{OH} and G_{H2O2}. The G_{eaq} for γ-radiolysis is in a good agreement with the reported values up to 200°C, but slightly lower at 250°C. The water decomposition gives a similar pattern with G_{eaq} yields. In the fast neutron radiolysis, although a similar change of the G-values with temperature was observed, the higher molecular products of G_{H2} and G_{H2O2} and the lower radical yield of G_H and, especially, G_{eaq} were determined. It was made clear that the LET effect still remains even at elevated temperatures. Concerning the experimental results, it is suggesting that the spur size would expand at higher temperatures and the fraction of the intraspur reactions decreases. Consequently, the amount radicals diffusing out from the spur increases. To confirm this suggestion, an additional experiment was made.
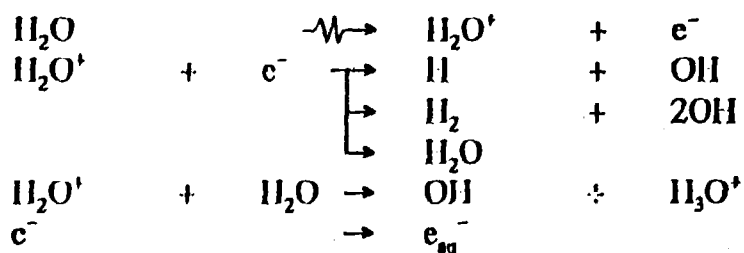
In order to clarify the characteristics of the determined G-values, computer simulations under the simplified conditions in nuclear reactors have been also carried out. The recent G-values for γ-radiolysis reported by Elliot, by Kent and Sims, and by us are nearly equivalent from the point of simulations. On the contrary, G-values for fast neutron radiolysis give a significant influence to the result, which arises from the higher molecular yields and smaller radical yields of water decomposition in fast neutron radiolysis, and it has been revealed that the dose evaluation in the reactor is inevitably important. In addition, it was pointed out by the simulations that reverse reactions for H_2 + ·OH → H· + H_2O and e_{aq}^- + H⁺ → ·H, which can be neglected at room temperature, become important at higher temperatures.

The model of initial intratrack chemical processes of water radiolysis

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According to current concept, the primary products of water radiolysis are radical-cation H_2O^+ and quasi-free electron e^- with energy lower than ionization potential of liquid water. In the conventional diffusion kinetic model, these species are supposed to transform into OH radicals, H_3O^+ and e_{aq}^- within 1 ps, and their diffusion are not accounted for. Whereas that model has succeeded to some extent, it cannot give any answers to the following problems; (i) small amount of solute(for example, NO_3^-) reduces the initial yield of e_{aq}^- as well as the yield of H_2, (ii) the origin of H_2.

Then, we think the importance of diffusion and reactions of H_2O^+ and e^-, and propose the model of initial chemical processes of water radiolysis, which contains the following reactions;

$$
\begin{array}{llllll}
H_2O & & \overset{\wedge\!\!\wedge}{\longrightarrow} & H_2O^+ & + & e^- \\
H_2O^+ & + & e^- \longrightarrow & H & + & OH \\
& & & H_2 & + & 2OH \\
& & & H_2O & & \\
H_2O^+ & + & H_2O \rightarrow & OH & + & H_3O^+ \\
e^- & & \rightarrow & e_{aq}^- & & \\
\end{array}
$$

This model has rather many parameters: diffusion coefficients of H_2O^+ and e^- which determine the upper limits of above rate constants, width parameters of initial distribution of H_2O^+ and e^- and the energy needed to produce a typical spur. However, we think it possible to determine such parameters by accounting for following; (i) reproducing the initial condition in the conventional model at 1 ps, (ii) explaining the decrease in the initial yield of e_{aq}^- in the presence of special solute such as NO_3^-, and considerable decrease in the yield of H_2 in the presence of such solutes. We examine the possibility of this model to explain experimental results, and report the calculated results.

Abstract was not submitted

MECHANICAL AND DIELECTRIC RELAXATION
OF RADIATION CROSSLINKED POLYMERS

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Mechanical properties of crosslinked polymer networks are usually characterized by their modulus plateau, related to the average molecular mass in-between crosslinks $\langle M_c \rangle$, and the Mooney Rivlin constants derived from stress-strain experiments. The distribution of M_c, however, is usually not studied. From the statistical theory of rubber elasticity it follows that distribution of M_c is related to the distribution of mechnical or dielectric relaxation times.

In this paper the effect of crosslinking on these relaxation time distribution spectra are discussed for natural rubber, polyethylene, polyvinyl chloride, unsaturated polyester resins and for some oligomer-monomer systems.

Relaxation time distributions are derived from mechanical stress relaxation and dielectric measurements using the Kohlrausch response function $\Phi = \exp[-(t/\tau)^n]$ which is found applicable to mechanical as well as electric actions. Exponent n of the Kohlrausch function characterizes the broadness of the distribution which, in turn, is related to the distribution of the inter-crosslink molecular mass M_c, while parameter τ is the temperature dependent average relaxation time. Computer programs were developed for determining distributions from results of time-domain, frequency domain and temperature domain mechanical and dielectric measurements.

The relaxation time distribution is found to broaden by increasing crosslink density, i.e decreasing $\langle M_c \rangle$ in the case of radiation crosslinked natural rubber above glass transition and polyethylene above crystalline melting temperature. In the case of oligomer-monomer mixtures the situation becomes more complicated because of the plasticizing effect of the monomer, but still tractable by the developed formalism.

FUNDAMENTAL ASPECTS OF SELECTIVITY OF THE RADIATION-INDUCED PROCESSES IN HYDROCARBONS AND RELATED POLYMERS

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The results of systematic studies of selectivity of radiation-induced effects in hydrocarbons, polymers, and microheterogeneous polymer systems irradiated at low temperatures (down to 10 K) are analyzed. Three principal aspects are considered:

(i) The selectivity of primary radiation-induced events in macromolecules and prototype hydrocarbon molecules. It was concluded that the selectivity of bond scission in many cases correlated with the structure and reactivity of the corresponding radical cations. Direct evidence for localization of the primary events at conformation defects were obtained for linear polyethylene (PE) irradiated at 15 K. This was explained by selective deprotonation of the primary hole from gauche position. The conformation of the parent molecule and association were found to control selective reactivity of the radical cations of alkenes, aromatic hydrocarbons, and related polymers.

(ii) The role of local molecular dynamics, which controls the selectivity of reactions in irradiated polymers under the conditions of inhomogeneous distribution of active species. In particular, selective intrachain recombination of the radical pairs in crystalline region of PE was found to occur at ca 65 K due to one-dimensional H-atom tunneling, which is replaced by classic interchain three-dimensional radical site migration in disordered amorphous region or at higher temperatures. Selective dynamic effects are generally significant for high-ordered systems or at low temperatures.

(iii) The peculiarities of radiation-induced processes in microheterogeneous polymer systems. These features were studied using a series of styrene-butadiene block copolymers with microdomain size of ca 10 nm and their homogeneous analogues. Positive hole transfer was found to occur only between neighbouring component molecules (units), whereas interdomain electron migration proved to be important for microheterogeneous systems.

Pulse Radiolysis Studies on the Polymerization of Acrylates and Methacrylates

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The real time kinetic analysis of high energy initiated polymerization is very difficult, partly because of the high rate of these reactions resulting in reaction times of the microsecond scale and partly because of the difficulties of detection under the hard conditions of the electron beam irradiatio. Pulse radiolysis together with kinetic spectroscopic detection seems to be a proper method to estimate kinetic parameters of high energy initiated polymerization [1]. By this method the actual radical concentration can be monitored and the actual average termination rate parameter [2] can be calculated.

The transient light absorption of pulsed electron beam irradiated cyclohexane solution of methyl acrylate (MA) and methyl methacrylate (MMA) were investigated. In both solutions a transient light absorption was observed with a maximum around 290 nm that was attributed to α-carboxyalkyl radicals. As the structure of the growing radicals does not change, the shape of the spectra measured at different time after the pulsewas found similar.

The values of second order rate parameters of termination k_t were determined as a function of dose for the two monomers and were compared.

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RANDOMLY AFFECTED KINETICS APPLIED TO REACTIONS OF CHEMICALLY ACTIVE SPECIES IN IRRADIATED CONDENSED MEDIA

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Fluctuations, static disorder and other external random impacts are known to be important factors affecting mechanism and kinetics of chemical reactions in condensed media. Such randomly affected reactions are discussed here in t ie framework of the general theory [1] covering the entire range of physical conditions making influence on processes of this kind. To illustrate the application of theoretical results to radiation chemistry, two particular aspects of the problem are considered in detail. They include the influence of static disorder on recombination kinetics of charged species in glassy solids [2] and the effect of stochastic surroundings on the monomolecular decay [3]. It has been shown that both processes cannot be adequately described in terms of classical (formal) kinetics. The latter is established to be one particular limit of the general theory proposed. Another limit corresponding to the so-called polychromatic approximation appears to be useful only at extreme low temperatures. It has been demonstrated that our approach seems to be useful for the unified description of geminate and homogeneous reactions, for studying the elementary step of charge carrier transport in polymer materials as well as for deducing statistical characteristics of stochastic media from experimental kinetic data.

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Irradiation of Polymers for Photoelastic Ivestigations

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The stressless fixation of three-dimensional states of deformation in polymers allows the
analysis of "special states" of elastic stresses even in the interior of complex constructional
units and machine parts. This is the reason for the fact that in spite of the development of
modern experimental methods of the analysis of deformation, which are in general restricted
to the deformation of the surface of the bodies, the classical "photoelasticity" is still an
adequate procedure for solving technical problems. However there are several restrictions on
the applicability of the presently used procedures. A potential way to overcome these
restrictions is the use of ionizing radiation, which in several polymeric materials causes a
more or less perfect fixation of three-dimensional states of deformation. The search for
suitable polymers includes the modification of well-known materials like epoxy resins
(Araldit B type) as well as the application and development of materials not yet used in this
field of engineering. Peliminary results of the search for such new materials are presented as
the Austrian contribuition to an international project, in which scientists from Hungary,
Croatia and Austria are co-operating.

24

PHYSICO-CHEMICAL PROPERTIES OF MEMBRANES OBTAINED BY RADIATION GRAFTING ONTO FEP FILMS

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Physico-chemical investigations were carried out on the membranes prepared by radiation-induced graft copolymerization of methacrylic acid and vinyl acetate individually and/or in binary mixtures onto poly (tetra-fluoroethylene - hexa-fluoropropylene) (FEP) films. The change in thermal properties of the polymeric substrates and graft copolymers was determined by differential scanning calorimetry (DSC). It was found that the prepared membranes possess good thermal stability and can be used at relatively high elevated temperatures. These membranes showed also good electrochemical and hydrophilic properties to elucidate the possibility of their practical use as ion-containing membranes.

ION-CONTAINING MEMBRANES OBTAINED BY RADIATION GRAFTING OF INDIVIDUAL AND BINARY MONOMERS ONTO POLYMERIC SUBSTRATES

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The preparation and characterization of different ionic and hydrophilic membranes, obtained by radiation grafting of individual and binary vinyl and acrylic monomers onto polymeric substrates, were carried out in this study. The post and direct radiation grafting methods were used as techniques for the membrane preparation processes. The effect of controlling factors and appropriate reaction conditions on the yield and homogeneity of grafting was investigated. The possibility of practical uses for the prepared membranes were investigated by measuring some of their selected properties such as thermal stability, electrical conductivity, swelling behavior and reverse osmosis properties (water flux and salt rejection).

Abstract was not submitted

EMISSION SPECTRA AND DECAY KINETICS OF PULSE IRRADIATED
POLYCRYSTALLINE TRYPTOPHANS

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Summary

Presented study has been performed mainly by pulse radiolysis method without external analytical light but with the measurement of light emitted by the irradiated sample. On the background of usuall Cerenkov light, the non-Cerenkov emissions were recorded, their decays analysed and spectra constructed. The general technique of pulse radiolysis of solid samples is in print as a monographic paper.

Contrary to the majority of biogenic amino acids, tryptophan shows, after the pulse of ionizing radiation, a comparatively long lasting phosphorescence with the maximum at 580 nm. The half life time of the main first order decay is 2.2 µs, the energy of activation in the range of 188-393 K is 0.026 eV/molecule. The pulse radiolysis picture of light emissions from solid tryptophan reveals also the steady state of well known singlet emission of tryptophan in UV (350 nm). The decay of it is fast, in the order of nanoseconds so that with microsecond resolution, this mode of fluorescence is observed only as the increment of Cerenkov emission during the pulse as a steady state concentration.

The origin of long lived emission from excited tryptophan is discussed (possibilities of excitation by Cerenkov radiation or by singlet emission mentioned above, as well as experimental attempts to excite the 580 nm emission by UV). The working hypothesis of mechanisms of observed phenomena looks for explanation by spurs in solids. The existence of such form of dissipation of ionizing energy is as real as in liquids; ca 30% of energy is deposited in spurs originating from more than one ionization. Therefore the main primary process of radiolysis of tryptophan is a single ionization of a molecule of tryptophan giving rise to singlet excitations. At least 30% of molecules taking part in the primary process are double or more ionized yielding double radicals or triplet states which decay slowly in comparison to singlets mentioned above.

The question why th 580 nm, ionizing radiation induced emission has not been observed yet may be answered that the crystalline state only may permit the specific excitation by high energy quanta and electrons. The occurence of the discussed emission in aqueous solutions is not possible, because multi-ionization spurs cause the formation of molecular products in water. Attack by radical products of water radiolysis may cause only singlet excitation, and H_2O_2 and H_2 from multi-ionization spurs are practically not reactive at all.

Presented phenomena exhibit unusual aspects of energy transfer in solids. L and D enantiomers give practically identical effects, just described, but the DL tryptophan racemate shows much weaker 580 nm emission. Consideration of basic differences between enantiomeric and racemate crystals, and higher density of the racemate may suggest radiationless deactivation in the latters. Closely packed molecules in the DL variety create better conditions for energy transfer, contrary to the enantiomere which emits energy as phosphorescence. The singlet emission is identical in L, D and DL varieties. Observed effect of difference in 580 nm emission has not a direct connection to chirality, but certainly an indirect one, because chirality determines completely different arrangement of molecules in the racemate.

Decomposition of Halogen Containing and Phenolic Compounds Related to Pesticide Pollutants of Surface Waters: Pulse Radiolysis Investigations

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Recent environmental control examinations have indicated that pesticides and products of their partial degradation falling under severe environmental protection regulations appeared in surface waters. These include non-biodegradable halogenated and/or phenolic compounds, not allowed to be found in rivers in detectable concentrations by using standard pollution control test methods.

The objectives of the present study were to contribute to finding free radical reaction pathways to eliminate dangerous pollutants from aqueous systems. Aromatic compounds substituted with Cl, Br and/or OH, C(O)CH₃ groups were used as models for pollutants. Oxidising and reducing free radicals were produced in the absence or presence of air/oxygen by subjecting aqueous solutions of the compounds to pulses of 4 MeV electron beams from a linear electron accelerator. Transients were detected by fast kinetic spectrophotometry.

Substituents effects on formation and decay of free radical intermediates are discussed in terms of the electron donating or withdrawing properties. The reactivity of free radicals and the state of protonation of substituted phenols is varied also by changing pH of the solvent, and these give rise to variations in the reaction mechanism.

29

MÖSSBAUER AND POSITRON ANNIHILATION STUDY OF OXYHEMOGLOBIN EXPOSED TO γ-RAYS AND ELECTRONS

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Preliminary analysis of oxyhemoglobin radiolysis was made by Mössbauer spectroscopy and positron annihilation technique.

Oxyhemoglobin in red blood cells irradiated by γ-rays with average energy of 15.5–16 MeV in doses of ~100, ~300 and ~600 kGy was studied by Mössbauer spectroscopy. It was found several products of oxyhemoglobin radiolysis which were related with deoxyhemoglobin, aquomethemoglobin, hemichromes and/or methemoglobin hydroxide, hematin and/or μ-oxodimers, and the high spin Fe(III) complexes formation. Basing on Mössbauer parameters the changes of these products versus doses were shown and possible pathways of oxyhemoglobin radiolysis were supposed.

Oxyhemoglobin in concentrated solution irradiated by γ-rays with average energy of 9 MeV in doses of ~16.5, ~22.5 and ~33.0 kGy was simultaneously studied by Mössbauer and positron life-time (PLT) spectroscopies. Mössbauer spectra showed oxyhemoglobin deoxygenation process only in contrast with red blood cells irradiation. Moreover, oxyhemoglobin deoxygenation versus doses appeared to be different in both cases. Parameters of PLT spectra varied with doses and likely characterized structural changes in protein molecules resulted from oxyhemoglobin deoxygenation and irradiation.

Oxyhemoglobin in concentrated solution irradiated by electrons with average energy of 10 MeV in doses of ~1, ~3 and ~5 kGy was studied by Mössbauer and PLT spectroscopies. Mössbauer spectrum of oxyhemoglobin irradiated with dose of ~5 kGy showed oxyhemoglobin deoxygenation and hemochromes formation. Parameters of PLT spectra of oxyhemoglobin irradiated in doses of ~1 and ~3 kGy appeared almost the same and their comparison with those of γ-irradiated oxyhemoglobin permitted to explain obtained results as the presence of oxyhemoglobin deoxygenation and some other structural changes in hemoglobin molecules.

The results of this study demonstrated variations of oxyhemoglobin radiolysis in red blood cells and solution as well as dependence of radiolysis process on the type, energy and doses of radiation.

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EFFECTS OF X- AND UV-IRRADIATION ON PROTEINS
I. PROBING THE STABILITY OF PROTEINS BY DIFFERENT TECHNIQUES

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The radiation damage of many proteins has been investigated in aqueous solution. The proteins investigated differed in their molecular characteristics, such as molar mass, number of subunits, amino acid composition, and nature of the active center in the case of enzymes. By various measures and additives (e.g., use of protectives and repair substances) we achieved modifications of the radiation action of X-rays and UV light.

For a comprehensive analysis of different radiation effects we had to apply a gamut of different methods of physical biochemistry [1-3]. By use of different techniques we succeeded in revealing numerous changes of the micro- and macrostructure of proteins as well as their functional ability. UV absorption, fluorescence, and CD spectroscopy unveiled changes of aromatic and other chromophores (e.g., heme group) and helix content of proteins; these methods were also able to indicate the formation of bityrosines and large aggregates, and to show the exposure of buried groups and the extent of unfolding. Enzymic tests allowed statements on the extent of inactivation and the success of repair attempts. Size exclusion chromatography monitored changes of the protein structure and the integrity of aromatics; when coupled to fluorescence detection, the method turned out to be a powerful screening technique for disclosing the protective efficiency of different additives. Electrophoreses allowed statements on fragmentation, unfolding and crosslinking of protein subunits. Small-angle X-ray and light scattering, densimetry, viscometry, and analytical ultracentrifugation reflected changes of the protein overall structure and the gradual progress of aggregation phenomena. Analytical methods of (bio)chemistry rendered changes of amino acids and special groups (e.g., SH and SS), and provided information regarding the occurrence of stable deleterious species (e.g., H_2O_2).

The parameters derived from various techniques were compiled, normalized, and presented in several correlation and stability plots, combining functional and structural properties of the proteins as well as the irradiation conditions. To allow clear-cut correlations of the radiation effects monitored by the different techniques, the derivation of several novel evaluation procedures was required.

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EFFECTS OF X- AND UV-IRRADIATION ON PROTEINS
II. THE MODIFICATION OF IRRADIATION OF THE ENZYME LYSOZYME

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The investigation of enzymes has a long tradition in radiation biology since enzymes are useful objects for studying both structural and functional changes caused by radiation. Enzymes containing SH or SS groups are calling for special attention [1-2]. Lysozyme is a widely occurring enzyme consisting of a single polypeptide chain. The tertiary structure of the enzyme is known, it is stabilized by 4 disulfide bridges. The molecule has a cleft which houses the active center; several amino acids (e.g., Ala, Asn, Asp, Glu, Trp) are involved in enzyme-substrate interactions.

For our experiments lysozyme was dissolved in dilute buffer and was irradiated with X-rays (0 - 20 kGy) or UV-C light (0 - 200 kJ·m⁻²) under a great variety of conditions. Several physico-chemical and biochemical techniques were applied for monitoring a series of different radiation damages, reflecting changes in primary, secondary, tertiary, and quaternary structure of the enzyme: e.g., change/ destruction of aromatic amino acids and cystins, inactivation, dimerization and aggregation, fragmentation, unfolding, decrease of helix content, etc. When using X-rays, some of the radiation effects intensified in the post-irradiation period.

Our investigations were focussed mainly on several modifications of the radiation conditions. A considerable influence was found by variation of dose, gassing conditions, enzyme concentration, nature and concentration of additives. The additives screened comprised many radical scavengers, reductants and oxidants including reduced and oxidized forms of thiols as well as common antioxidants and antioxienzymes, inorganic salts, chelating agents, drugs, etc. Many ·OH scavengers, thiols, thiourea, dithionite, ascorbate, NADH, NAD⁺, and EDTA protected the enzyme effectively against X-irradiation. Some of the compounds exhibiting absorption in the UV range, such as thiourea, ascorbate, NADH, and NAD⁺, turned out to be potent protectives against UV light. The different protective efficiency of the additives against X- and UV-irradiation is due to differences in the primary reactions caused by these two types of radiation. Results were summarized in dose-effect curves and several correlation plots. Normalization of the molecular parameters allowed a quantitative comparison of the radiation damages registered by different techniques and of the protective efficiency provided by different additives.

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EFFECTS OF X- AND UV-IRRADIATION ON PROTEINS
III. THE INTERACTION OF RADIATION WITH EYE LENS PROTEINS

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The lens of the eye has the function of focussing light entering the eye on the retina. The lens is a transparent tissue made up largely of proteins called the crystallins, the remainder being essentially water. Three major classes of crystallins (α, β, γ) have been identified in mammalian lenses [1]. The molecular properties of the crystallins such as molar mass and thiol content vary considerably. Significant changes of the lens proteins can occur as a consequence of aging and irradiation, finally leading to several pathological alterations of the lens including cataractogenesis [2,3].

The examination of lens proteins damaged by nonionizing and ionizing radiation is of particular interest for many fields of research (radiation biology, medicine, pharmacology, etc.). There is some evidence that the occurrence of holes in the ozone layer of the atmosphere as well as X-irradiation may lead to an enhanced formation of human cataracts. Therefore the investigation of irradiated lens proteins and the search for radioprotective substances is of pressing importance at the present time.

Our investigations are concerned with the radiation interaction (UV light, X-rays) with the crude extract and individual fractions of calf lens crystallins in aqueous solution. Experiments made use of UV absorption and fluorescence spectroscopy, size-exclusion chromatography, SDS-PAGE, determination of SH and SS content, etc. Several radiation damages could be registered (destruction of aromatic amino acids and cysteins, aggregatio1 phenomena, etc.), the effects depending on the crystallin class and the nature of radiation used for the investigation. The radiation effects could be influenced by the irradiation conditions (e.g., oxic or anoxic solution, presence of certain additives). Especially a variety of different classes of additives were applied, allowing a systematic search for efficient radioprotectants against both sorts of radiation. We succeeded in finding various substances protecting the crystallins effectively against UV light and/or X-irradiation, some of them being also of medical relevance.

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RADIATION-INDUCED EFFECTS IN PROTEIN-RICH ORGANIC MATTER THE THIN FRACTION OF EGG WHITE

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Preservation of the nutritional and organoleptic characteristics of protein-rich natural products during radiation sterilization is the primary technological problem of the foodstuff industry. Further, under natural conditions, protein components of the living organisms are permanently exposed to damages by free-radical species originating from normal cell metabolism, as well as from natural sources of radioactivity and UV portion of the solar spectrum. Consequently, unveiling of the mechanism underlying genesis of these impairments is of equal significance for industrial aspects, as for the understanding of the fundamental biological processes such as aging and carcinogenesis. For the mentioned studies, we chose the model system of hen egg white thin fraction, whose composition is well defined and which proved suitable for viscosity measurements. Also, comparative studies were undertaken using aqueous ovalbumin solutions of various concentrations.

The N_2O saturated thin fraction of egg white was irradiated using a γ-source of ${}^{60}Co$ in the dose range up to 60 kGy. Analysis of the radiation produced damages of protein components was performed by discontinuous SDS-polyacrylamide gel electrophoresis (SDS-PAGE) and viscosity was measured using an Ostwald viscometer at $20°$ C. SDS-PAGE revealed that both kinds of protein damages, scissoring and crosslinking, took place, the former being more pronounced. The G-value varied with the dose applied and was estimated to be 0.25 at 10 kGy. The abrupt initial viscosity decrease in the dose interval up to 6 kGy was attributed to the degradation of composite structure through the hydrogen bonds cleavage. Further increase in the radiation dose resulted in the gradual increase in viscosity owing to the crosslinking of the egg white proteins. The initial value was reached around 50kGy. On the contrary, 10 times diluted, irradiated egg white samples showed the absence of initial abrupt decrease in viscosity. This observation pointed out that the egg white composite structure was destroyed on dilution, releasing most of the bound water molecules. The sample persisted marked crosslinking and the gel dose was estimated to be 70 kGy. Further, the viscosity of 1% solution of purified ovalbumin increased with the dose in a step-function manner. The corresponding gel-electrophoretogram indicated that the ionizing radiation caused marked crosslinking and minute scissoring of ovalbumin. Radiation initially caused dimerization with the G-value dependent on the dose applied. Further irradiation causes generation of larger agglomerates (trimmers, tetrameres etc.) whose molecular weights exceeded 1 MDa at a dose of 3kGy. The crosslinking process was continued up to the protein condensation. The respective gel-dose was estimated to be 8.5 kGy. It is pertinent to note that the measured egg white protein damages were one order of magnitude smaller than expected from the radiolysis of aqueous solutions of its purified constituent.

Air saturated egg white samples were irradiated in the same dose range. It was found that the overall G-value was 0.3. Egg white ovalbumin was more damaged under the air than under N_2O saturation conditions. The dominant process in that case was scissoring. Opposite to the N_2O saturated egg white samples, the air saturated ones were fragmented to discrete molecular weight species indicating strict peroxy radicals discrimination of protein epitops in the scissoring reaction. The air saturated samples showed the similar initial decrease in viscosity coinciding with the N_2O samples viscosity decrease.

Compilation of the results obtained in our study enabled proposition of criteria discriminating contribution of direct versus indirect radiation effects on the studied protein damages. Also, we proved the existence of the protective mechanism and explained to details the resulting impacts.

IDENTIFICATION OF IRRADIATED INSECTS: CHANGES IN THE MIDGUT OF THE CONFUSED FLOUR BEETLE, TRIBOLIUM CONFUSUM DUV., INDUCED BY GAMMA RADIATION

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At the doses of ionizing radiation suggested for a quarantine treatment, death of insects and mites is generally not immediate. Alive pests may be present in the agricultural commodities for several days. This can be a disadvantage if the product is for immediate export and there is a nil insect requirement. Shipments of these agricultural products may be rejected when alive pests of quarant..ie importance are found. A simple test is needed to ensure the quarantine personnel that the pest of quarantine importance has been irradiated and it does not pose a quarantine risk.

Development of a practical technique for the identification of irradiated pests was recommended by the ICGFI Task Force Meeting on Irradiation as Quarantine Treatment (Chiang Mai, Thailand, 17-21 Febr. 1986).

The midgut is the main site for digestion and absorption of the products of digestion. Thus, it is a very active tissue metabolically. The old epithelium is replaced by new cells produced by the regenerative nidi. Regenerative cells are very sensitive to radiation. Damage of them results in loss of the midgut epithelium in irradiated insects.

The following changes in the midgut structure of the confused flour beetle were observed: (1) destruction of regenerative nidi; (2) elongation and enlargement of epithelial cells; (3) vacuolization of the epithelial cells; (4) fading of cell boundaries in the epithelium; (5) damage of nuclei (chromatin grains scattered throughout the cytoplasm of epithelial cells); (6) loss of the brush border; and (7) desintegration and further loss of the epithelium. The most pronounced effect of irradiation treatment was the destruction of regenerative cells of the midgut. Their destruction by radiation prevented the replacement of the secretory cells of the epithelium. As a result, the epithelium disappeared and the gut lumen enlarged. Causes other than ionizing radiation producing disintegration of the epithelium in the midgut of insects are unknown. Because the degenerative changes in the midgut are positively correlated with both dose and time elapsed after irradiation exposure, a pathological syndrom of irradiation effects on the midgut may be used for a rapid and efficient method of identification of irradiated insects.

DETECTION OF IRRADIATED FRUITS BY GAS-CHROMATOGRAPHIC METHODS

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To detect the irradiated fruits with applied low doses (0.5-30 kGy), two methods of chromatography (GC-MS and LC-LC-GC) were used to determine the radiolysis compounds of lipids after irradiation such as alkanes and alkenes. Extraction of volatile hydrocarbons was done from some parts of irradiated fruits e. g. flesh part (avocado), seeds (papaya) and kernels (mango and apricot).

The analysis of hydrocarbons by GC-MS proved the suitability of using C17:1, C16:2, C15:0, C14:1 as markers for irradiated avocados even 0. 75 kGy. Same indicators appeared in analysis of irradiated papayas and mangoes with 1.5, and 3.0 kGy. Also, C15:0, C14:1, C16:3 can be used to identify the irradiated apricots with low dose (0.5 kGy).

The detection of alkenes was only improved by a more selective isolation e. g. dienes or trienes by LC-LC-GC-FId. Through few minutes the irradiated apricots and avocados with low doses (0.5, 0.75 kGy) respectively can recognize with the products as C16:2, C17:2, C16:3 without interfering peaks.

In all cases, using C16:1, C16:2, C16:3 besides significant amounts of C17:2 can be use as markers for irradiated fruits.

COMPARATIVE STUDIES BETWEEN FUMIGATION AND IRRADIATION OF SEMI-DRY DATE FRUITS

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This experiment was carried out on Egyptian semi-dried date fruits "El-Seidie CV." which use to process paste of dates. It is aimed to compare the effect of irradiation (1.5, 3.0 kGy) and fumigation with methyl bromide (MB) on physical, chemical and mycological characters especially production of aflatoxins during storage the dates for long time (8 months).

Irradiation was more effective in de-infestation of dates than MB, but caused significant loss in weight of dates. No changes were observed in irradiated samples as well as in MB samples for moisture content, pH-values and titratable acidity but less significant changes were observed in browning and sugars, either total, reducing or sugar/acid ratio.

Irradiation (3.0 kGy) was more effective than other treatments for inhibition the growth of fungi and prevention of aflatoxin production in synthetic borth media or date fruits.

Therefore, irradiation dose (3.0 kGy) can be recommended to use than fumigation (MB) to keep date fruits with good quality, free from infestation, contamination and more safe for human consumption during long storage period.

DETERMINATION OF RADIATION STERILIZATION DOSE OF HEALTH CARE PRODUCTS BASED ON ISO STANDARDS

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The use of ionizing rediation for the steriliz- ation of health care products has increased during the last 30 years. The choice of sterilization dose depends on three parameters, namely the bioburden, the radiosensitivity of microorganisms and the assurance of sterility required. The terms of sterility represents an absolute condition in which no life-form is present. It is also clear that no existing system can detect such an absolute condition therefore sterility or non-sterility represents always a theoretical probability. ISO "Sterilization of health care products - Validation and routine control - Gamma and electron beam radiation sterilization" standard recommends various methods which can be used to determine the radiation sterilization dose for a chosen sterility assurance level. All methods recommended in this standard require sterility testing of samples of product, that have received lower doses of radiation than the final sterilization dose. Sterilization dose was calculated by "Dose Setting Using Bioburden Information " for hypodermic needles, occlusive dressing material and hydroxy-apatit (dental implant). Sterilization doses for these products were 16.6 kGy, 15.1 kGy and 19.5 kGy, respectively. We calculated the sterilization dose for hypodermic needle by "Dose setting using fraction positive information from incremental dosing to determine an extrapolation factor". This method has offered us 15.04 kGy sterilization dose at SAL 10^{-6}.

RADIATION TREATMENT OF PHARMACEUTICALS

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The ionizing radiation is widely used for sterilization of disposable medical products and supplies. The advantageous experiences have given considerable possibility for radiation treatment of pharmaceuticals too, particularly where conventional sterilizing processes have been proven inadequate. Because of the sensitive chemical structure of most drugs and basic materials difficulty arises that undesirable chemical and physical changes may accompany the radiation treatment. The most crutial point is the radiation dose for the treatment. The choice of the dose depends on the bioburden, the desired final microbial count, the radiosensitivity of bioburden and the chemical stucture of the materials. Following the new recommendations of ISO and AAMI the real possibility arises to work out product specific dose setting procedure for different kind of pharmaceuticals.

Some heat sensitive enzyme powders were investigated (Pancreaton, Neopancreatin, Duodenum) to carry out feasibility study of radiopasteurization treatment for these row materials. The initial count was ranging between 10^1 - 10^6 microorganisms/g and some samples contained spore formers too, having D_{10} values of 0.843 - 1.798 kGy. The radiation dose to reduce the initial contamination level to 10^2 microbes/g was found between 12-15 kGy. The protease, amylase and lypase activity of irradiated samples were also tested and its reduction were found within the acceptable level.

Product specific sterilizing doses were worked out for Aprotinin solution and Heparin according to ISO Method 1. (Dose setting using bioburden information) recommendations. Regarding the required sterility assurance level (SAL:10^{-6}) the sterilizing dose for Heparin was found to be 24.7 kGy and for Aprotinin 11.0 kGy. The biological activity of samples irradiated by calculated doses were tested according to FIP directives and USP XXII. Some reduction was found in the activity, but all of the irradiated samples comfirm to the acceptable level.

Dose setting procedure for pharmaceuticals differs from those, applied for disposable medical products. Determination of product specific dose should regard all of the physical, chemical and biological parameters which could influence the quality of the radiation treated medical products. Adapting the new ISO, AAMI standards for medicinal products will meet the requirement of GMP and it can help in the widespread application of this technology in industrial scale.

The Role of Partitioning of Reagents in Grafting and Curing Reactions Initiated by Ionising Radiation and UV

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Grafting and curing processes initiated by ionising radiation (cobalt-60 and electron beam) and ultraviolet light (UV) are now extensively used in industry. In the inks and coatings fields particularly, radiation curing is growing rapidly in importance. Grafting and curing are related processes, the time scale of events being one of the parameters which separates the two systems. Grafting reactions can proceed over a time scale from seconds to days, whereas curing processes occur in a fraction of a second. In grafting, a chemical bond is formed between polymer and substrate whereas in curing, the cured polymer film is usually bonded to the surface being coated by essentially physical forces. However there is the possibility that concurrent grafting with curing can also occur, leading to products with unique properties. Currently, even though radiation processing is being used commercially, there is a need to expand basic research into the relevant chemistry of oligomers and monomers used in such systems, particularly curing. In both grafting and curing, there is also a need to shorten reaction times such that substrates are exposed to a minimum of radiation. In this respect, the use of additives to accelerate grafting and curing reactions is important.

In the proposed paper, new additives found to enhance grafting initiated by ionising radiation and UV will be discussed, using styrene as model monomer with cellulose and polypropylene as representative backbone polymers. The role of certain of these additives in accelerating analogous curing processes will also be examined. A novel mechanism to explain the reactivity of these additives in grafting initiated by ionising radiation and UV will be discussed in depth. The mechanism involvers the concept of partitioning of reagents during reaction. Extension of the concept to curing processes will also be considered. The use of the theory in predicting additive effects in practical applications of grafting and curing will be evaluated.

CALORIMETRIC STUDY OF CATIONIC PHOTOPOLYMERIZATION

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The photopolymerizaton of penta-erythritol tetra-glycidyl ether (initiator Degacure KI - 85, a 50 % solution of bis -(diphenylsulphonio) -phenylsulfide bis-hexafluorophosphatein in propylene carbonate) was studied at different temperature and initiator concentration by a du Pont 910 type differential scanning calorimeter equipped with a 2.4 mm thick quartz window on the top of the calorimeter body. The heat flux at given time is taken to be proportional with the global instantaneous rate of polymerization.

RESULTS

1, According to isothermal calorimetric studies during irradiation the heat flux increases rapidly after light-on then, through a maximum, decreases approaching zero.
The heat flux versus time curves exhibit a marked temperature dependence: the maxima are shifted to shorter time with increasing temperature and increase up to a certain temperature (t_{max})
At higher reaction temperatures the maxima of the flux curves decrease.

2, The decay curves obtained after switching the light off are found to be exponential. These decay curves also exhibit a marked temperature dependence; as the temperature increases, the heat flux decreases more and more rapidly approaching zero. At lower temperatures the heat flux decreases slowly. At higher temperatures by interrupting the radiation anywhere the heat flux decays rapidly to zero.
By switching the light on the heat flux increases again.

From our experimental results the following conclusions can be drawn:
1, During the polymerization reaction the lifetime of the initiating centers are long compared to the lifetime of free radicals in case of radical polymerzation.
2, The rate of deactivation of the initiating centers increases with increasing temperature.

The shape of the isothermal heat flux curve can be described by the following equation
$$- dM/dt = k_n\ C(0)(k_i/(k_d-k_i))(\exp(-k_i t) - \exp(-k_d t))M(0)\exp(- k_n\ C(0)(k_i/(k_d-k_i))$$
$$((1-\exp(-k_d t) /k_d)-(1 -\exp(-k_i t))/k_i\ )$$
where C(0) = initial initiator concentration

      M(0) = initial monomer concentration

      k_n = rate constant of the monomer consumption

      k_i = is the rate constant of the formation of the initiation centers

      k_d = rate constant of the decay of the initiation centers

The rate of polymerization after switching off the light is:
$$-dM/dt = (-dM/dt)_s \exp(- k_d t_s) \exp(- (k_n\ I_s/k_d)(1-\exp(- k_d t_s)))$$
where M_s = monomer concentration at the time of switching off the light

      I_s = is the initiation center's concentration at the time of switching off the light

      t_s = elapsed time after the switching off the light

      $(-dM/dt)_s$ = polymerization rate at the time of switching off the light

Thermomechanical investigations of UV cured epoxy coatings

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In this study the thermomechanical properties of UV cured epoxy coatings were investigated. The aim was to establish the dependence of the thermomechanical features of the irradiated samples from the temperature of UV curing, the elapsed time after the irradiation and from the photoinitiator concentration.

Epoxy polymers were obtained by UV irradiation at 366 nm of the samples previously applied in a thin layer on a polyester film and covered with a quartz glass. The UV source used was a UVIX low pressure mercury lamp produced by Desaga GmbH.

The glass transition temperatures (Tg) of the irradiated samples were measured by a Du Pont Thermomechanical Analyser.

We have found that the Tg values of the samples increase with the storage time, the phenomenon which we explain by the post-polymerisation of the irradiated samples. The samples also became more homogenous after several days in the dark due to the post-polymerisation.

ENERGY DISTRIBUTION OF SLOW ELECTRONS IN A HARD-SPHERE LIQUID

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Energy fluctuations in a hard-sphere liquid is calculated for differently-sized subsystems. The absolute deviation of the total energy of a subsystem from the average, as a function of the size of the subsystem, is seen to exhibit a maximum in the range of about three times the hard core radius. This result, together with the distribution function also evaluated, implies that the only energy exchange process which fluctuations can effect between the liquid and a H-like atom, is the excitation from the 3-rd to the 4-th Rydberg state. The relevance of this result to the ion-electron recombination probability in irradiated or illuminated nonpolar liquids is discussed.

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POSITRON ANNIHILATION IN LIQUID NORMAL HYDROCARBONS

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Systematic positron lifetime studies were made in normal
hexane, octane, decane and dodecane vs. temperature in the range
10 - 85 °C. Lifetime spectra contain $1 - 3 \cdot 10^7$ events; they were
evaluated by assuming exponential decay with constant parameters
for each annihilation channel. Evaluation was made with and with-
out source correction: increasing effect of source correction on
the positron parameters was found for increasing alkyl chain
length.

Experiments indicate that positron decays significantly
in four annihilation channels with characteristic lifetimes
around 0.12, 0.35, 1 and >3 ns. Properties of lifetime- and rela-
tive intensity functions vs. temperature suggest that the 0.9 and
>3 ns components correspond to different decay mechanisms of o-Ps.
The nature of the variation of these two lifetimes vs. temperature
is similar to that found in the molar volumes of the $-CH_2-$ and
$-CH_3$ groups, respectively. The probability of positronium formation
was found to increase in each system with temperature.

Since lifetimes and relative intensities are results of
complicate thermalization-, ionization- and electron/positron/po-
sitronium transport processes that strongly and, as recently, un-
predictably depend on the microscopic structure of the liquid, we
abstrain from giving even a qualitative explanation for the ir-
regular trends shown vs. alkyl chain length.

Radical Reactions in the Radiolysis of Cyclopentane

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The C_5 and C_{10} end products produced in the gamma radiolysis of cyclopentane were investigated at very low total doses (25 - 50 krad) in the presence and absence of iodine radical scavenger. The hydrocarbon products as well as the iodine containing compounds formed indicate the following main radical species: cyclopentyl G=4.9, 1-pentyl G=0.2, cyclopentenyl G=0.07, and H atom G=1.3 radicals/100 eV. About 79% of the cyclopentyl radicals react in the bulk medium with a disproportation to combination ratio of 0.97. The 3-cyclopentenyl radicals decay in reactions with cyclopentyl radicals forming cyclopentyl cyclopentene as the primary product. The 1-pentyl radicals end up a n-pentane, 1-pentene, and n-pentyl cyclopentane. Radical precursors account for about 50% of the total end product yields which is much smaller than found in the radiolysis of cyclohexane and cyclooctane. The radiolysis mechanisms for the three cycloalkanes are compared and discussed. A general scheme is used to describe the hydrogen and alkyl radical formation in all three compounds.

Heavy Ion Radiolysis of Cyclooctane
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The variation in the yields of the major end products produced in cyclooctane have
been used to probe the radiation chemical effects of the track structures of gamma rays, 1
- 10 MeV protons (LET 47 - 12 eV/nm), and 5 - 20 MeV helium ions (LET 147 - 72
eV/nm). Iodine scavenging techniques were used to show that in gamma radiolysis 70% of
the cyclooctyl radicals survive until about 10 microseconds and therefore react in the bulk
solution. For 10 MeV protons (LET = 12 eV/nm) only 41% of the cyclooctyl radicals
survive until these times and the value drops to 8% for 10 MeV helium ions (LET = 106
eV/nm). With increasing particle LET there is significantly more reaction of the radicals in
the track. The yield of bicyclo[3.3.0]octane (pentalane) was also found to be dependent on
particle LET. This cross bridged product is produced exclusively by the unimolecular
decomposition of the excited singlet state of cyclooctane. The yield of the singlet state
probably decreases with increasing LET because of an increase in cross combination
reactions of the electron-cation pairs in the particle track.

INFLUENCE OF LINEAR ENERGY TRANSFER ON
REACTIONS OF CYCLOALKYL RADICALS

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The ratios of differences of yields of cycloalkanes to yields of bicycloalkyls produced by gamma- and alpha-irradiation are generally independent from the molecular mass of cycloalkanes and from the LET (up to 200 eV nm^{-1}). Transient spectra of cycloalkyl radicals of C_5–C_{10} cycloalkanes obtained by electron pulse radiolysis were measured. The reaction rate coefficients of combination of cycloalkyl radicals and yields of bicycloalkyls are ring size and strain dependent.

ELECTROLUMINESCENCE IN ORGANIC SOLIDS

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The electroluminescence in organic solids, a phenomenon of basic and practical interest, was discovered by Helfrich and Schneider in anthracene crystals almost thirty years ago[1]. In 1987 Tang and VanSlike realized a novel organic electroluminescent device[2] having high electroluminescent emission efficiency, fast response, low voltage drive and simplicity of fabrication. This result was the stimulus for an increasing interest in this topic among the scientists. Since then, many different materials and device configurations have been proposed. In this communication the state of the art in this field and some preliminary results obtained in our Institute will be briefly presented.

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8th Tihany Symposium

Uncertainty of dose measurements in radiation processing

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The major standard organizations of the world have addressed the issue of reporting uncertainties in measurement report and certificates. There is, however, still some ambiguity in the mind of many people who try to implement the recommendations in real life. This paper is a contribution to the running debate and presents the authors view, which is based upon experience in radiation processing dosimetry. The origin of all uncertainty components must be identified and can be classified according to type A and type B, but it is equally important to separate the uncertainty components into those that contribute to the observable uncertainty of repeated measurements and those that do not. Examples of the use of these principles are presented in the paper.

RADIATION CHEMICAL REACTIONS OF TRIPHENYL TETRAZOLIUM CHLORIDE IN LIQUID AND SOLID STATE

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Tetrazolium salts are known as possible dye agents for radiochromic dosimeter films. An example is 2, 3, 5-triphenyl-tetrazolium chloride (TTC), since its irradiation results in the formation of the pink coloured triphenyl formazan in aqueous or alcoholic solutions.

The radiation chemical behaviour of TTC has been studied both by electron pulse and gamma radiolysis. In the course of the pulse radiolysis investigations the fast formation of an intermediate product, absorbing at around 360 nm, was observed under both oxydizing and reducing conditions. In the latter case i. e. in deoxygenated solution, however, the formation of the formazan, absorbing at around 490 nm, was observed probably through a quinonoid type intermediate due to a radiolytic reduction process.

Due to this radiation chemical phenomenon a polyvinylalcohol-based TTC film containing radiochromic dye was produced and tested for dosimetry purposes. A suitable concentration of the components gave a measurable response in the 1-100 kGy dose range by evaluating the irradiated 100 um thick TTC film at 493 nm, i. e. at the peak of the absorption maximum. Several investigations, such as the study of the effect of light, dose and dose rate, irradiation temperature and humidity, have been carried out to characterize this film system with respect to its potential practical application.

MEASUREMENTS OF ELECTRON DEPTH-DOSE DISTRIBUTION
IN THICK PLASTICS AND EFFECTS OF ACCUMULATED CHARGE

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When an electrically non-conducting plastic block is irradiated with electrons, whose range is less than the block thickness, these electrons come to rest within the material after expending all their energy. These electrons are trapped within the material, except for those near the surface which leak out. This stored negative charge peaks near the end of the electron range and creates an electrostatic field within the material.

The influence of such a field on the dose distribution has been a subject of many research papers in past with sometimes contradicting conclusions. McLaughlin[1], Harrah[2] and Tanaka et al.[3] have reported shortening of the electron range. Mehta ... reported an increase in the peak/surface dose ratio in PMMA for a particular irradiation geome. ... the other hand, Janovsky and Miller[5] did not observe any appreciable effect on the depth-dose distribution in PMMA. Also, using the intrinsic properties of polyethylene as a dosimeter, Janovsky et al.[6] have recently shown that there is no significant effect of accumulated charge on the dose distribution in polyethylene. With the recent availability of 10-MeV linacs larger pieces of plastic are being electron-processed; thus, a thorough understanding of this effect is urgently needed.

In the present study, we have conducted several experiments in an attempt to clarify these seemingly contradicting results. We have measured the depth-dose distribution in polyethylene and PMMA for a scanned electron beam from the 10-MeV/1-kW linac under typically radiation processing conditions. Three different irradiation geometries were studied: a horizontal stack of plastic sheets interleaved with film dosimeters; and a thin strip of the dosimetric material along the beam axis sandwiched between two vertical stacks of plastic sheets and also between two solid blocks of plastic. Other variables were the surface dose and the radiation history of the plastic.

We have observed that the measured depth-dose distribution depends on the irradiation geometry; for certain geometries, the effect on the dose distribution of the accumulated charge is significant. Also, the extent to which the observed distribution is affected depends on the absorbed dose and the material. A hypothesis is offered that attempts to explain the seemingly contradicting results; it is based on the shape of the electrostatic field present in the non-conducting plastic due to the accumulated charge.

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Abstract was not submitted

DESKTOP REPETITIVE SOURCES OF POWERFUL ELECTRON BEAMS, X-RAY AND MICROWAVES FOR LAB INVESTIGATIONS ON RADIATION CHEMISTRY, PHYSICS AND BIOLOGY

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The Report presents the results of an implemented research and development program that has made it possible to create compact repetitive sources of powerful electron beams, X-ray and microwaves. The basic unit of such devices represents the high-voltage repetitive driver RADAN 303B which permits one to generate 4-nanosecond accelerating voltage pulses energized the vacuum diodes (direct-action accelerating tubes) based on the explosive-emission cathodes. For the laboratory investigations it is only needed that specific parameters of the e-beam, x-ray and microwaves be high. Our practice has shown that, in most of lab's experiments , the driver's stored energy of up to 5 J is quite sufficient. It is energetically profitable to increase the average power by using a repetitively operating devices.

The backbone of the high-voltage driver is a fitted Tesla transformer with an open core made of a steel. The driver is a Blumlein generator and comprises a high-pressure gas spark gap. The output voltage with a 150-Ohm accelerating tube can be controlled at a range of 30-300 kV. So, the maximum peak power of the e-beam generated exceeds 500 MW. The special designed connection-to load module permits mounting sealed-off and evacuating x-rays tube and e-beams tube, as well as k-band back-wave oscillator by the user himself.

Sealed-off industrial-made e-beam tube permits to inject the dense (up to 1 kA/cm^2 across the foil window of 1 cm^2 area) e-beam through thin beryllium foil into ambient air. The accelerator allows the connection in parallel of two tubes. Two-e-beam device is necessary for the double-side treatment of polymeric film samples, biological objects, and for the surface sterilization. We used a specially designed calorimeter to measure the e-beam energy absorbed by a sample. This value is about 0.1-0,2 J per pulse and corresponds to 1-2 W average power. Such energy absorption permits one to rich a lethal dose for number of microorganisms for a few seconds. We also presents another source of high-current e-beam, as follows: ribbon-beam diode. This device permits to increase the accelerator's efficiency because of the matched operation mode of the ribbon diode and high-voltage driver. So, the the peak electron current arriving through the Al-Be foil window was as high as 300 A/cm^2 while the beam's area was 0,5 x 11 cm^2. The average ribbon e-beam power exceeds 40 W when operation at reprate 25 p.p.s..

The biological and likes object's response with a non-thermal shoot of the powerful microwave can be studied when applied relativistic back-wave oscillators (frequency region 35-70 GHz). These oscillators can generate the nanosecond microwave pulses at a peak power as high as 10 MW both in single and repetitive mode. The strength of the electrical fields of output microwave ranges from 10 kV/cm up to breakdown value for a ambient air (of 100 kV/cm for the nanosecond pulse duration).

Our recently developed devices meet the below listed autonomy requirements:
- operation safely and local protection from the accompanying x-rays;
- small overall dimensions and no special requirements to supply lines;
- ease to operate and maintain and readiness to operate at any time.
The commercial versions of RADAN-devices may be of interest for those research groups that by any reason, have no access to unique and expensive superpowerful facilities.

OXIDATION OF BENZOQUINONE BY RADIOLYTICALLY PRODUCED OH RADICALS

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In the present study we have used product analysis and time resolved absorption spectroscopy to examine the mechanism for attack of radiolytically produced OH radicals on benzoquinone in aqueous solution. It is found that OH radicals add to benzoquinone at a diffusion controlled rate. The initial adduct, which has a lifetime of ~500 ns, eliminates a proton to form an anion which subsequently undergoes electron transfer with the benzoquinone to produce benzoquinone radical anion. This semiquinone radical then disproportionates to produce hydroquinone as a by product. Reaction is essentially quantitative. The studies described here illustrate the power of radiation chemical reactions, particularly those involving radical intermediates.

REDOX CHEMISTRY OF SOME PHENYL THIYL RADICALS

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Rates and equilibria for electron transfer between para substituted phenoxyl radicals and phenyl thiylate anions in the following reaction:

$$X\text{-}C_6H_4\text{-}O\cdot + X\text{-}C_6H_4\text{-}S^- = X\text{-}C_6H_4\text{-}O^- + X\text{-}C_6H_4\text{-}S \qquad (1)$$
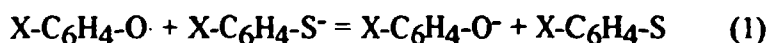
have been investigated by pulse radiolysis. Examination of the rates in terms of the Marcus theory indicates that the reorganisation energies are similar for H-, CH_3- and CH_3O- as para substituent. However, for H_2N- and O^--para substituents the reorganisation energies are larger. These observations are in accord with structural information from resonance Raman and ESR studies of the radicals.

Reduction potentials for the phenyl thiyl radicals, $E^o(X\text{-}C_6H_4\text{-}S\cdot / X\text{-}C_6H_4\text{-}S^-)$, were derived from the equilibrium constants of reaction (1) and the known reduction potentials of the phenoxyl species, $E^o(X\text{-}C_6H_4\text{-}O\cdot / X\text{-}C_6H_4\text{-}O^-)$. Both of these reduction potentials decrease as the electron donating power of the p substituent rises. However, the effect is much stronger for the oxygen-substituted species. This is also true for $D_{O\text{-}H}$ and $D_{S\text{-}H}$ the gas phase bond dissociation energies of the two types of radical. These observations demonstrate that the interaction between the oxygen atoms and the aromatic ring system is much greater than that which occurs with the sulphur atoms.

Abstract was not submitted

A Pulseradiolysis Study of the OH Radical Induced Autoxidation of Methanesulphinic Acid

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Methanesulphinic acid, CH_3SO_2H, reacts with OH radicals at pH 7 forming CH_3SO_2 radicals with a rate constant of $(6.0\pm1.0)\times10^9$ $M^{-1}s^{-1}$. The CH_3SO_2 radical absorbs at 325 nm with an extinction coefficient of 900 ± 100 $M^{-1}cm^{-1}$ and disappears in a second order self-reaction with k = $(1.0\pm0.2)\times10^9$ $M^{-1}s^{-1}$.
This radical reacts with oxygen forming a peroxyradical which absorbs in the UV below 300 nm. The peroxyradical reacts in turn with methanesulphinic acid reforming the CH_3SO_2 radical whereby a chain oxidation of sulphinic acid takes place. During the course of the chain oxidation a peroxyacid, presumably methaneperoxymonosulphonic acid, is formed and accumulated. This acid absorbs in the UV and eventually decays by reaction with excess methanesulphinic acid (or hydrolysis).The final product of the chain autoxidation is methanesulphonic acid. The chain is very efficient and proceeds until either oxygen or methanesulphinic acid is exhausted. The mechanism is compared to the chain autoxidation of sulphite.

REACTION OF DIETHYL MALEATE AND DIETHYL FUMARATE WITH HYDRATED ELECTRONS AND HYDROXYL RADICALS

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The reaction of two dicarboxyl acid esters the diethyl maleate (cis, DEM), and the diethyl fumarate (trans, DEF) with hydrated electrons and hydroxyl radicals were investigated in dilute aqueous solutions in the whole pH range.

The rate constant of electron capture for both esters are 2.2×10^{10} $mol^{-1}dm^3s^{-1}$, which is in the diffusion controlled range. The intermediates formed in the electron capture reaction of DEM have an absorption maximum at 340 nm. The shape of the spectra obtained in higher and lower pH range were found slightly different due to the protonated and unprotonated form of the intermediates. DEM^- reversibly protonates with pK = 5.2. For DEF we obtained similar electron adduct spectrum, but the pK_a of DEF^- is below 4. The electron adducts decay in second order reactions.

The hydroxyl radicals add to the double bond of DEM and DEF with a rate constant of 5.9×10^9 $mol^{-1}dm^3s^{-1}$. During this reaction δ-carboxy-alkyl radicals form with absorption maximum at 300 nm, the ε_{300nm} extinction coefficient is 400 $mol^{-1}cm^{-1}$. In alkaline solutions the spectra were found changing in time, and below 300 nm remaining absorbance was observed. This remaining absorbance is due to the ionized form of oxalacetic acid ethylester with absorption maximum at 270 nm, and ε_{max} is 12000 $mol^{-1}dm^3cm^{-1}$. In acidic solutions the OH adducts decay without remaining absorbance, with second order kinetics.

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59

RADICAL IONS OF OLIGOSILANE AND POLYSILANE

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In order to examine electronic properties of polysilane Si-Si skeleton, the radical ions generated by γ-irradiation of polycyclo-hexylmethylsilane and polymethylphenylsilane have been studied by means of the electron spin resonance (ESR) and electronic absorption spectroscopic methods. The ion radicals of permethyloligosilanes [$Si_n(CH_3)_{2n+2}$, n=4~6] have also been studied for comparison.

Polysilane and oligosilane samples were synthesized by Wurtz-type reaction and purified by distillation (oligomers) or repeated pre-cipitation (polymers) from chloroform solution. The average number of Si in the polymer main chain was approximately 80. The radical anions were generated by irradiating deaerated 2-methyltetrahydro-furan solutions of polysilane or oligosilane at 77 K or 4.2 K with ^{60}Co γ-rays. The radical cations were generated by irradiating the samples in Freon mixture ($CFCl_3$:$CFBr_2CFBr_2$=1:1) solution in the same way.

The radical anions of both oligosilanes and polysilanes gave a similar absorption spectrum composed of a UV band (ca. 4 eV for oligomers and 3 5 eV for polymers) and an IR band (1.5-2 eV for oligomers and 0.8 eV for polymers). The polysilane radical anions show an axially-symmetric ESR spectrum with $g_\perp$=2.0023 and $g_\parallel$=2.0064. These results are explained by an unpaired electron of the polymer radical anions occupying a pseudo-π(p) orbital composed of anti-bonding Si-Si and antibonding Si-C orbitals. It is strongly suggested that the polymer radical anion is localized on a pre-existing defect probably composed of an elongated Si-Si bond, while the oligomer radical anion is delocalized over the Si-Si skeleton. It is also shown that the positive hole of the polymer cation radical is loca-lized on Si-Si σ-orbital(s) corresponding to the σ-bonding orbital of the intact polysilane, while the positive hole is delocalized on the whole Si-Si skeleton in the oligomer.

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Gamma-Ray Induced Crystallization of Oxide Glass, Nitrate Glass and Egg-White Glass

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Crystallization of inorganic glass takes place by ^{60}Co γ-ray irradiation at room temperature. X-Ray diffraction (XRD) pattern of calcium gallate glass, $60CaO \cdot 40Ga_2O_3$, irradiated with γ-rays of 10^7 Gy indicates a precipitation of CaO, Ga_2O_3 and $CaGa_4O_7$ phases *etc.*, whereas heat treatment at 760-780 $^{\circ}$C for 50-100 min results in a precipitation of thermally stable $CaGa_2O_4$ phase which has a CaO/Ga_2O_3 ratio of unity. An Ar^+-laser irradiation of $60CaO \cdot 40Ga_2O_3$ glass for 32 s under the output power of 1.0 w results in a formation of the $CaGa_2O_4$ phase and thermally metastable $Ca_3Ga_4O_9$ phase which has a CaO/Ga_2O_3 ratio of 60/40. This ratio is the same as that of $60CaO \cdot 40Ga_2O_3$ glass. It is considered that the γ-ray induced crystallization takes place as a result of "decomposition" of three-dimensional network structure composed of covalently bonded GaO_4 tetrahedra, to which Ca^{2+} is ionically bonded at interstitial sites. The ^{57}Fe-Mössbauer spectra prove the crystallization, since Fe^{3+} is substituted for Ga^{3+} and forms the network structure. Crystallization results in a quantitative decrease in the optical transparency in the IR region, as was observed in aluminate and tellurite glasses.

Nitrate glass, KNO_3-$Sr(NO_3)_2$, is comprised of a random packing of K^+, Sr^{2+} and NO_3^-. The XRD pattern of γ-ray (5×10^3 – 5×10^5 Gy) irradiated nitrate glass is similar to that of heat-treated KNO_3-$Sr(NO_3)_2$ glass. The FT-IR spectrum of γ-ray irradiated KNO_3-$Sr(NO_3)_2$ glass, especially the stretching vibration of $K-ONO_2$ bonds, is sensitive to the crystallization. An egg-white glass prepared by drying egg-white gel undergoes a crystallization by the γ-ray (10^6 Gy) irradiation at room temperature and also by the heat-treatment at 60 $^{\circ}$C for 10 – 210 min. The XRD pattern indicates that the crystalline phase is matched with the "hypothetical structure A" proposed for β-keratin by Huggins (1980).

RADIATION-CHEMICAL SYNTHESIS OF MONOCHLOROEXCHANGED METHYLCHLOROSILANES

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Radiation-chemical method of production of monochloroderivatives methylchlorosilanes as compared with the known ways of synthesis allows to increase the yield of end-used product by 1, 5-2 times, the high selectivity being remained. The process is proceeding at low temperature under pressure of 2-4 atms. The steam pressure of initial methylchlorosilanes decreases by 5-6 times as compared with the known methods of synthesis. The increasing of the yield of monocloroderivatives reduces the volume of recirculated initial product and decreases the amount of wastes

Compound	Conversion by initial product, %	Monochloro-derivative, %	Polichloro-derivative, %	Selectivity
CH_3SiCl_3	5.03	4.23	0.79	0.84
$(CH_3)_2SiCl_2$	21.5	18.1	3.4	0.84
$(CH_3)_3SiCl$	21.5	19.0	2.1	0.90

The synthesis of chloromethylthreechlorosilane was carried out by using a pilot plant. The process is estimated as ecologically pure.

SCAVENGING OF ELECTRONS AND RADICALS IN FROZEN CHLORIDE-ALCOHOL GLASSES

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Chloride-alcohol glasses frozen at 77K and irradiated with γ-rays produce the stable primary products: Cl_2^- and e_t^- which could be measured spectrophotometrically. The products have been mobilized by increase of temperature particularly in the presence of scavengers. In the case of e_t^- light is also a very efficient mobilizing factor. Such processes with added scavengers: p-nitrosodimethylaniline (pNDA), p-benzoquinone (pBQ), hydroquinone (HQ), chromates and nitrates have been examined using both temperature and light as a mobilizing factor. The kinetics of electron photobleaching as well as electron scavenging efficiences of the above scavengers have been studied. It has been shown that these efficiences could be ordered in the following sequence: pNDA(acid)>pBQ>chromate>pNDA(neutral)>nitrate>>HQ.

RADIATION EFFECTS ON ALUMINUM AND HYDROGEN DEFECTS IN NATURAL QUARTZ

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Aluminum and hydroxyl defects in crystalline quartz are known to directly affect the performance of a quartz containing device in a number of industrial applications. Hydrogen whic is found in all quartz [1] in the form of OH^- molecules trapped at different defect sites influences nearly every application of the material. Al^{3+} is found at substitutional Si^{4+} sites. Al^{3+} therefore needs a charge compensation which is provided by monovalent alkalis. Electrodiffusion (sweeping) under hydrogen ambient removes the $Al-M^+$ (where M^+ is either Li^+ or or Na^+) centers and produces $Al-OH^-$ centers which shoe a near infrared absorption at 3306 and 3367 cm^{-1}. Natural crystals exhibit both $Al-M^+$ and $Al-OH^-$ centers in their as received state. H-sweeping also removes the $Al-M^+$ centers and increases the strength of $Al-OH^-$ centers in thelimit to compensate all the aluminum with hydrogen [2]. Irradiation beyond 200 K converts the $Al-M^+$ centers into a mixture of Al-hole and $Al-OH^-$ centers [3]. Thus, during irradiation the elastic modulus c′ which represents a type of interatomic force constants, undergoes a change due to modification of impurity related defect centers. The hydroxyl defects act as a source of hydrogen to replace alkalis at Al^{3+} with H^+ ions [4]. In the present work, we have used our near infrared absorption results obtained upon irradiation at 77 K before and after 300 K-irradiation on good quality alkali- and H-swept natural quartz with similar Al·and widely different alkali and H levels. Using the irradiation cycle and defect dynamics consideration, a quantitative estimation of Al-M , Al-OH and Al-hole defect centers has been presented. The results would have a direct application in evaluating the contribution of these centers separately in the total transient and steady state frequency offset in natural quartz resonators due to passage of radiation through the bulk of the material. Such studies are of direct industrial and space applications.

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RADIATION EFFECTS ON HYDROXYL DEFECTS IN Ge-DOPED QUARTZ

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Radiation effects in quartz resonators are known to be due to the presence of impurities. Trivalent aluminum is the most pervasive impurity that replaces the tetravalent silicon substitutionally. Another impurity known to substitute the silicon sites is the tetravalent germanium. While the contribution of Al-centers in the radiation response of quartz is well studied, such effects on Ge-centers has been less studies. However, most commercial quartz contains both Ge and Al in varying proportions. Recently, we have shown that the Ge-doped quartz can be differentiated with the conventionally grown quartz by using the near infrared absorption [1]. It has been shown that the Ge-doped quartz exhibit the presence of 3481 cm^{-1} band which has been related to the presence of Ge in quartz lattice. At high Ge concentration (3000 ppm) another small band at 3656 cm^{-1} was found to occur. In this paper, we report our results on radiation induced modification of hydroxyl defects in these crystals. Irradiation was done in a sequence at 77 K, 300 K and finally again at 77 K. Irradiation was done using a van de Graaff electrostatic accelarator of Okalhoma State University. A detailed description of irradiation and measurement techniques is available from a previous paper [2].

The results show that at the stage of 300 K-irradiation, the 3481 cm^{-1} band in the as grown Ge-doped quartz is completely removed and a new radiation-induced band at 3525 cm^{-1} is observed. This band is expected to represented a possible configuration of $[GeO_4e-/Li^+]^o$ center with a proton in the vicinity. The Al-OH$^-$ bands produced after irradiation show a larger long-bond to short-bond (Al_1/Al_s) intensity ratio in the Ge-doped quartz than that usually observed in the conventionally grown cultured quartz crystals.

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Some Aspects of Bromine Atom Chemistry.

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Rate constants of hydrogen abstraction reactions between the bromine atom and several hydrogen donors, RH, were determined in water, using Br⁻ and promethazine as monitor substances. Comparison of the aqueous rate constants with those measured in acetonitrile and some alcohols reveals the hydrogen abstraction rate to be largely unaffected by the polarity of the solvent. In particular, the reaction does not utilise the potential rate enhancement that would result were the free energy gain of HBr dissociation in water to lower the transition state. Thus, the rate-determining step of the reaction seems to produce molecular HBr. For a number of oxygen-containing organic substrates the aqueous rate constants were found to display an excellent linear correlation with the equilibrium constants of the hydrogen abstraction reactions. However, at similar thermochemistry the rates for alkanes are significantly lower than those for alcohols and similar heteroatomics. This was interpreted in terms of a polar transition state, where the ionisation potential of the radical, R·, rather than that of the parent RH, is the main descriptor of charge transfer component. The finding of the absence of noticeable solvent effect on the rates suggests that the act of hydrogen transfer may be too fast for the solvent to adapt to the polarisation of reacting species traversing the reaction path.
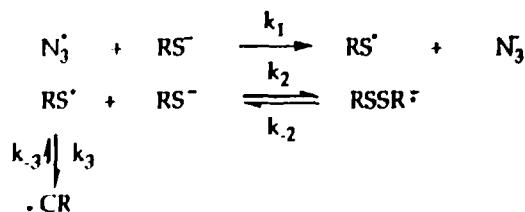
On the Kinetics of One Electron Oxidation of Thiols and Hydrogen Abstraction by Thiyl Radicals from α–Amino C–H Bonds

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Abstract

One electron oxidation of cysteine, homocysteine and glutathione by azide radical in alkaline solution (pH 10.5), where both the amino and SH groups are deprotonated, has been investigated by pulse radiolysis. Reducing α–aminoalkyl radicals ·CR ($H_2N-\overset{\overset{\textstyle CO_2^-}{|}}{C}-R$) which are formed via intramolecular rearrangement of thiyl radicals was detected using methylviologen (MV^{2+}) as oxidant in the kinetic analysis. The general scheme of the reactions is sketched as:

$$N_3^· \; + \; RS^- \; \underset{k_2}{\overset{k_1}{\longrightarrow}} \; RS^· \; + \; N_3^-$$

$$RS^· \; + \; RS^- \; \underset{k_{-2}}{\overset{}{\rightleftharpoons}} \; RSSR^{·-}$$

$$\underset{k_{-3}}{\overset{k_3}{\updownarrow}}$$

$$·CR$$

Thiyl radicals either equilibrate with $RSSR^{·-}$ in reaction 2, or undergo intramolecular transformation via equilibrium 3. At pH 10.5, equilibrium 3 is completely shifted to the right resulting in α–aminoalkyl radical formation. The rate constants in the reaction scheme for cysteine, homocysteine and glutathione were measured. With the rate constants obtained, the decay kinetics of $RSSR^{·-}$ into ·CR was simulated and it agreed with the one measured at 420 nm. At pH 10.5 the first order rate constants for the transformation (k_3) were determined to be 2.5×10^4, 1.8×10^5 and 2.2×10^5 s^{-1} for cysteine, homocysteine and glutathione, respectively. The rate constants for intermolecular hydrogen abstraction by thiyl radicals from α–amino C-H bonds of alanine and glycine were determined at the same pH to be 7.7×10^5 $M^{-1}s^{-1}$ and 3.2×10^5 $M^{-1}s^{-1}$, respectively. Thermodynamic estimation places the reduction potential $E^o(H_2NC(CO_2^-)CH_3^·, H^+/H_2NCH(CO_2^-)CH_3)$ at ca. 1.22 V, which implies a rather weak tertiary C-H bond in the anion of α-amino acids. Thus an intramolecular hydrogen abstraction mechanism for the transformation of thiyl radical to α–amino carbon-centered radical is postulated. Molecular geometry plays an important part in deciding the transformation rates (k_3) of different thiyl radicals.

Studies on Laser-Induced Photoionization of Tris-2,2'-bipyridyl Ru(II) Complexes in Polyelectrolyte Solutions.

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Many photophysical and photochemical studies have been reported on the tris-2,2'-bipyridyl Ru(II) complex as it can act as mediator for the photodecomposition of water using solar light [1]. Studies in micelles, polyelectrolytes etc. also have been carried out with the aim of slowing down the back reaction between the redox products formed. We observed a strong increase in the (biphotonic) photoionization yield of the Ru(II) complexes in the presence of polyanions viz. polymethacrylate and polyvinylsulphate compared to that in neat water. The results are reported in this paper. Tris-2,2'-bipyridyl Ru(II) chloride from Aldrich, sodium polymethacrylate from Polymer Standard Services and potassium polyvinyl sulphate from Aldrich were used. Solutions were prepared in water cleaned by a Millipore system and pH~9.3 was adjusted by the addition of NaOH. On photolysis of a 3.75×10^{-5} mol dm^{-3} solution of Ru(II) complexes in water by a 347 nm light flash emitted from a ruby laser, at high light intensity, the hydrated electron absorption was observed as has been reported earlier [2]. On addition of sodium polymethacrylate or potassium polyvinyl sulphate (2×10^{-3} mol dm^{-3}) the yield of the hydrated electrons increased by 140-150% compared to 45-50% in anionic micelles [2]. Also the halflife of the hydrated electrons increased nearly 5 times. At pH~9.3 the binding of the Ru(II) complexes to polyanions is electrostatic in nature. It was observed for the first time that binding of cationic Ru(II) complexes to polyanions causes a strong increase in the photoionization yield. The reason for increased photoionization might be partial charge neutralization of the complexes bound to polyanions with the consequence of a change in the ionization potential. Lithium chloride added to solutions containing Ru(II)-complexes and polyanions was found to decrease both the yield and lifetime of hydrated electrons. This is probably due to the fact that Ru(II) complexes are displaced by Li$^+$ ions. The released complexes are less ionizable and possess a higher reactivity towards the hydrated electrons than the bound ones.

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2. S.J.Atherton, J.Phys.Chem., 88 (1984) 2840.

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RADIATION, ITS NATURE, INTERACTIONS AND POTENTIAL APPLICATIONS
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The subject of radiation covers an immense range of scientific interests, from the basic question, what is radiation, how does it interact, with materials and how can this be modified and controlled then onto potential uses in such varied fields as physics,(as in semiconductors) through radiation chemistry with such well-tried applications as polymer modification and grafting or selected chain reactions and on to radiobiology where we may expect both basic research leading to a better understanding of the processes involved and to radiobiological applications such as sterilisation and then to medical appplications with the production of novel materials to meet new objectives.

In all this vast arena one must take fullest advantage of the unique properties of high energy radiations, such as the immense range of intensities and penetrations together with the mapping, of surfaces and depth possible with a fine electron beam of controlled voltage and beam pattern.

I do not feel that the field of potential applications has yet been sufficiently explored. How many experts in biological and medical developments who know the required aims and objectives know what new powers the radiation technique can confer; and how many radiation physicists and chemists are familiar with these very practical and highly desirable objectives

A few examples will be given of where an increased overlap between radiation physicists and chemists with biologists and medical experts may be highly desirable. We know what is accepted as a lethal dose and also have at least an approximate idea of the number of chemical reactions this dose may produce. What is in fact the sensitive species modified by this dose? How does it select one of these very vulnerable sites? Or is the lethality due to some simple mechanism already studied in polymer research eg random crosslinking or scission of DNA? Much of the required information and techniques is already available from our simpler polymer studies but not yet transferred across

By irradiating polymers in a suitable solvent such as water we can produce swollen gel structures with a wide range of properties, even within the same specimen. Can we find a medical or biological need in which this ability can be utilised

Many of us are familiar with laser light and claim to understand its fundamental nature. It can be used to initiate macromolecular reactions already closely studied with high energy radiation. Parallel work with laser light and the analysis and comparison of products may provide us with a deeper understanding of the real physical nature of the laser and the multiphoton reactions to which it can give rise.

We can go back even further and query the nature of radiation itself and the two physically contradictory models, wave or particle to which it has given rise. Each individual unit must show both very extensive wave properties as in radio waves and be able to react with individual molecules requiring it to have subatomic dimensions.. This wave/particle inconpatibility has been a major problem in present-day physics.

It is intended to raise a number of these considerations in the lecture and especially elicit a summary of the remarkable and often unexpected features which can be utilised in future radiation applications.
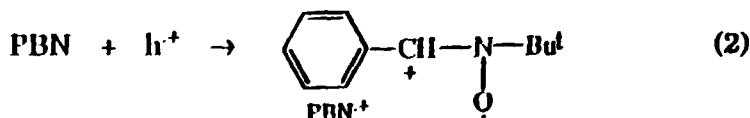
Radiation-chemical peculiarities of spin trapping.

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The application of spin trapping in radiation chemical studies makes it possible to identify short-lived radicals and thus provides a deeper insight into radiolysis mechanisms. Using time- resolved pulse radiolysis and pulse photolysis techniques as well as EPR, we have shown that the spin trap α-phenyl-N-tert-butylnitrone (PBN) efficiently scavenges short-lived primary radical precursors in the radiolysis of polar and nonpolar systems. It is shown that solvated electrons in aqueous or alcoholic solutions react, [eqn.(1)], dissociatively with the spin trap PBN (α-phenyl-N-tert-butylnitrone) forming the anion-radical O^- and N-*tert*-butylbensaldimine [PhCH=N-Bu^t]:

$$\text{PBN} \quad + \quad e_{solv.} \quad \rightarrow \quad O^- \quad + \quad PhCH=N\text{-}Bu^t \quad (1)$$
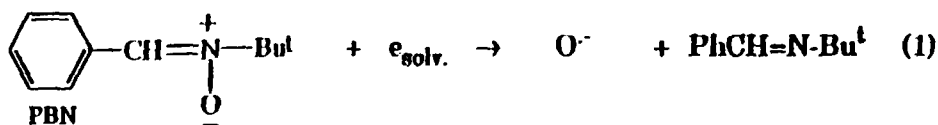
In the pulse radiolysis of PBN solutions with nBuCl as solvent, or by low temperature γ-irradiation in alkyl halide matrices spin trap PBN will be ionised by solvent derived positive holes in an electron transfer reaction (2):

$$\text{PBN} \quad + \quad h^+ \quad \rightarrow \quad \text{PBN}^{\cdot+} \qquad (2)$$

PBN$^{\cdot+}$ was characterised by its absorption spectrum (λ_{max}=420 nm in nBuCl) and by low temperature EPR. Being an α-nitroxylcarbenium ion PBN$^{\cdot+}$ reacts, [eqn.(3)], with various nucleophiles (Nu$^-$) forming stable nitroxide radicals:

$$\text{PBN}^{\cdot+} \quad + \quad Nu^- \quad \rightarrow \qquad (3)$$

Nu$^-$=H$_2$O, Cl$^-$, PBN
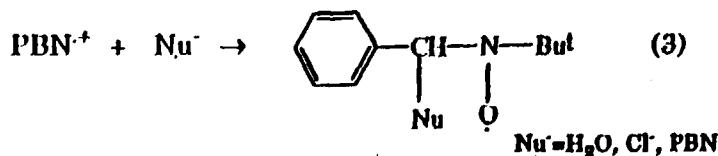
The observed reactions of the spin trap PBN with primary transients of radiolysis are of importance in spin trapping applications in both radiation chemistry and biology.
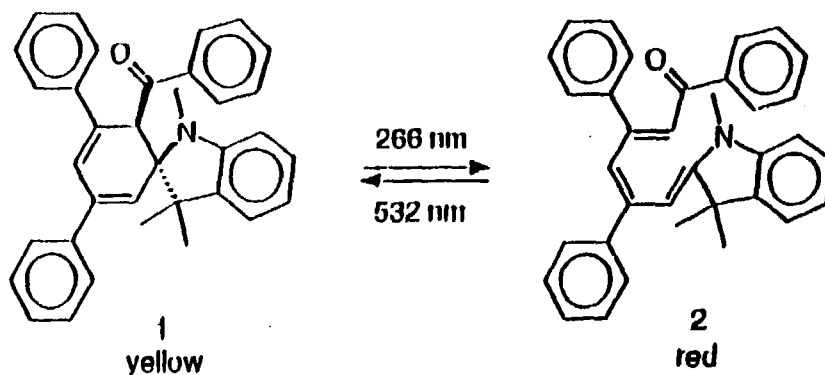
Photochroism of a New Spiroindoline Compound

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Spiro[indoline-pyrans] are known to be photochromic compounds and are anticipated to be useful as materials for reversible data storage[1].

The spiro[cyclohexadiene-indolines] (like 1) with a related structure represent a new class of spiroindoline compounds and are easily synthetized by ring transformation of 2,4,6-triarylpyrylium salts with 1,3,3-trimethyl-2-methyleneindoline[2]. They undergo reversible photoisomerisation to a merocyanine dye (2) on irradiation with light.

1
yellow

266 nm
532 nm

2
red

In laser flash photolysis experiments ring-opening and photobleaching reactions have been investigated and are found to be dependent on the solvent used. Ring-opening competes with intersystem crossing to the lowest triplet state and is even in nonpolar solvents like cyclohexane the only reaction pathway.

[1] B. L. Feringa, W. F. Jager and B. de Lange, *Tetrahedron* **49**, 8267 (1993)
[2] T. Zimmermann and M. Pink, *J. Prakt. Chem./Chem.-Ztg.* (in press)

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RADIATION-INDUCED DEGRADATION OF ALKANE MOLECULES IN LOW-TEMPERATURE MATRICES.

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The radiation-induced degradation of n-alkane molecules in rare gas matrices irradiated with fast electrons at 15-17 K was studied by IR spectroscopy in order to identify the basic pathes of hydrocarbon molecular ions and excited states conversion in rigid inert media. The charge and/or energy transfer to hydrocarbon solute was found to be very efficient in rigid argon and xenon matrices, which results in high yields of parent alkane molecules degradation at matrix:solute mole ratio ca 500:1. Trans-vinylene and vinyl alkenes, methane, and other short alkanes were detected as principal products of radiation-induced destruction of pentane and heptane molecules in rare gas matrices immediately after irradiation at 15 K. Some transient bands, which decay upon annealing the sample to 30-45 K (in argon) or to 60-90 K (in xenon), were also observed.

The primary processes were found to be essentially different in argon and xenon . In particular, C-C bond scission in alkane solute molecules in argon matrix is more efficient. This was explained by the difference of ionization potentials (IP) of the matrix molecules, which results in different population of excited ionic states of the hydrocarbon molecules. It was suggested that the ground electronic state of the parent radical cation of alkane was mainly populated as a result of charge transfer in xenon matrix (IP = 12,1 eV), whereas electronically excited cations of alkanes were formed in argon (IP = 15,75 eV) due to excess energy in highly exothermic charge transfer process in this matrix. In the latter case an excited cation dissociates even in rigid medium at very low temperature.

Irradiation of alkanes in xenon matrices containing electron scavengers (carbon tetrachloride, Freon-113) at 15 K leads to less efficient destruction of hydrocarbons. Possible identification of transient bands and the fate of primary cations are discussed.

NONTHERMAL ELECTRON SCAVENGING IN n-HEXANE

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The radiation-chemical yield of Cl^- ions resulting from a dissociative electron attachment to chlorobenzene has already been used as a measure of scavengeable electron yield in radiolysis of liquid. The competition between chlorobenzene and a secondary scavenger can be used to discriminate the reactions of nonthermal and thermalized electrons. At higher concentrations of secondary scavenger the reactions of thermalized electrons are completely supressed and the competition between thermalization and nonthermal electron scavenging by both scavengers takes place. By extrapolating the concentration of the secondary scavenger to zero, the ratio of thermalization and attachment can be obtained, as well as the ionization yield.

The present work was carried out in deaerated solutions of chlorobenzene in n-hexane. Nitrobenzene was used as a secondary scavenger. The concentration of radiolytically produced chloride was measured spectrophotometrically.

The ionization yield of 2.93 was obtained. Taking the value of $9 \cdot 10^{-12}$ s (9 ps) for thermalization time in n-hexane, the rate of dissociative electron attachment to chlorobenzene follows as $3.1 \cdot 10^{12}$ dm^3 mol^{-1} s^{-1}.

Redox Chemistry of Substituted Anilines

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Anilines can easily be oxidised by radiolytically formed one-electron oxidants, e.g. $N_3\bullet$ and $SO_4\bullet^-$. The primary product is aniline radical cation (reaction 1) which can deprotonate yielding anilino radical (reaction 2).

$$PhNH_2 \rightleftharpoons PhNH_2\bullet^+ + e^- \qquad (1)$$

$$PhNH_2\bullet^+ \rightleftharpoons PhNH\bullet + H^+ \qquad (2)$$

Thus the aniline radical cation is characterised by its one-electron reduction potential, $E^\circ(PhNH_2\bullet^+/PhNH_2)$, and its pK_a. These properties have been determined for a number of substituted anilines in aqueous solution by means of pulse radiolysis with optical detection. The major reference substance used in the reduction potential measurements was promethazine and the pK_a determinations were based on the spectral differences between aniline radical cations and anilino radicals. Using thermodynamical cycles the N-H bond dissociation energies of the corresponding anilines were calculated from the one-electron reduction potentials and the pK_a:s.

The effects of ring substituents on the aniline radical cation one-electron reduction potentials and pK_a:s as well as on the aniline N-H bond dissociation energies were found to follow linear free energy relationships (equation 3).

$$a = b + \rho^+\sigma^+ \qquad (3)$$

a in equation 3 denotes the reduction potential, pK_a or bond dissociation energy, b is a constant, ρ^+ describes the substituent dependence and σ^+ is the Brown substituent constant. These relationships were also found to fit into a family of linear free energy relationships holding for the one-electron reduction potential of arbitrarily substituted benzene radical cations and for the X-Y bond dissociation energy of arbitrarily ring substituted molecules with the general formula Ph-X-Y, respectively.

Charge Transfer to a Semi-Esterified Bifunctional Phenol

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Phenol radical cations are very unstable species and have not been observed before, with the exception of the radical cation of p-aminophenol [1]. In polar solutions, phenol radical cations are easily deprotonated so that only the phenoxyl radicals can be detected. However, in non-polar systems (alkanes, alkyl chlorides) it should be possible to generate these species by electron transfer from phenols (ArOH) to radiolytically formed solvent cations [2].

$$RH^{\bullet +} + ArOH \rightarrow RH + ArOH^{\bullet +} \rightarrow RH_2^+ + ArO^\bullet \quad (1)$$

Nevertheless, even under these conditions, in the case of monofunctional phenols, only phenoxyl radicals have been found.

During our studies of the stabilizer action modes of sterically hindered phenols, we performed charge scavenging experiments (1) with 2-tert-butyl-6-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-4-methylphenyl acrylate (Sumilizer GM®), a substance used industrially as a stabilizer for polybutadiene [3].

GM
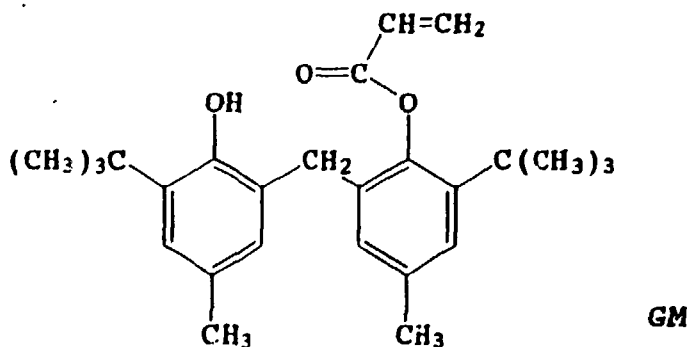
In the pulse radiolysis of GM in butyl chloride solutions , we found two species of *cationic origin - a phenoxyl radical and a radical cation localized at the acrylate group.* The phenoxyl radical was generated according to reaction (1) in a concentration range in which ionic processes dominate (c<0.02 M). Small amounts of ethanol removed it, and the acrylate cation also. The latter species decays by charge neutralization, presumably forming radicals which react subsequently with the intact phenol group and thereby producing more phenoxyl radicals.

The same reactions are observed in the case of similary structured bifunctional stabilizers, and give some insight into the ionic processes taking place in phenols with more than one functional group.

[1] R.H. Schuler, Q. Sun and G.N.R. Tripathy, J.Phys. Chem. **94** (1990) 6273
[2] O. Brede, R. Mehnert and W. Naumann, Chem. Phys. **115** (1987) 279
[3] S. Yashigo et al., Polymer Degrad. Stab. **22** (1988) 53

ION-MOLECULE REACTIONS STUDIED BY NUCLEAR DECAY TECHNIQUE. TRITIATED NAPHTHYLIUM IONS

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Naphthylium ions generated by β nuclear decay of 1,4 bitritionaphthalene[1,2] were allowed to react in the gas phase with benzene, and benzene/MeOH mixture.

The reaction was studied at benzene pressures ranging from 5 to 60 torr, in the presence of a thermal radical scavenger [O_2]. The effect of a gaseous base [$(CH_3)_3N$] and of an inert gas (Ar) on the reaction were also investigated.

The naphthylium ions react with benzene in the gas phase, yielding α and β phenylnaphthalenes, whose ratio markedly increases with the pressure of benzene and the concentration of the base. At the higher benzene pressures, and in the presence of the base, the isomeric composition of the products appears to be kinetically controlled and corresponds to a $\alpha{:}\beta$ ratio ~5.75. This value reflects the remarkable positional selectivity of the gaseous naphthylium cations.

Furthermore, the naphthylium ions display a significant substrate selectivity, as indicated by a kBenzene/kMeOH ratio ~1.2 in the competition experiments.

The mechanism of the gas phase naphthylation will be discussed.

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2, G. Angelini, Y. Keheyan, E. Lilla, G. Perez: Isomerization and self-condensation reactions ubsequent the β-decay of tritiated naphthalene in the presence of liquid and gaseous benzene, Radiochimica Acta 51, 173, 1990

Free radical chain oxidation of Fe^{2+} by hydroperoxides

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Hydroperoxides are decomposed by ferrous ions with a concomitant oxidation of the latter into ferric ion:

$$ROOH + Fe^{2+} \rightarrow RO^{\bullet} + Fe^{3+} + OH^-$$
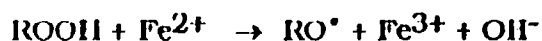
In the absence of a reducing agent for ferric ions, chain oxidation of ferrous ions occurs as a result of the subsequent reactions with alkoxyl radicals $RO^{\bullet}$ and other oxidizing secondary radicals ensuing in the interactions of alkoxyl radicals and the medium.

The amount of ferric ions formed was measured as thiocyanate complex in a chloroform methanol (2:1) mixture. Hydrogen peroxide (R = H) produced 2.0 molecules of ferric thiocyanate per molecule of H_2O_2; alkyl and aryl hydroperoxides gave about 3 molecules of complex, while fatty acid hydroperoxides produced more than 4 molecules of ferric thiocyanate complex per molecule of hydroperoxide.

These results are contrary to the expectations based on radiation chemistry experience: hydroxyl radicals generated from H_2O_2 would be expected to be most reactive and therefore least selective. However, 2.0 molecules of ferric thiocyanate produced per one molecule of H_2O_2 can be explained as if hydroxyl radicals reacted exclusively with Fe^{2+}:
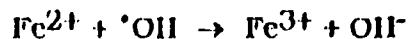
$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^-$$

STABILITY OF TRAPPED ELECTRONS IN THERMALLY MODIFIED ALCOHOL - ALCOHOL AND ALCOHOL - WATER GLASSES

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Absorption spectra of e_t^-, DTA and dielectric losses measurements of frozen irradiated matrices of different composition alcohol-water and alcohol-alcohol have been studied as a function of temperature.

In the system ethylene glycol -water and glycerol-water with more than 50% of water content the increase to maximum and then decay of e_t^- absorption has been observed. The strong decay of e_t^- always takes place before the system reaches the glass transition temperature.

On the basis of DTA and particularly dielectric losses measurements one can assume that the electrons have been trapped on specific aggregates composed with molecules of water and ethylene glycol or glycerol. The increase of temperature brings about the retrapping of electrons that is measured as the increase of electron absorbance.

The phenomenon has not been observed for other composition of alcohol-alcohol or alcohol-water thermally modified glasses.

The modelling of radiation-induced hydroperoxidation in solid systems

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There is a formal parallelism between autoxidation and radiation-induced oxidation of lipids if primary products, lipid hydroperoxides (LOOH), are followed with time and irradiation dose, respectively. The accumulation of LOOH is proportional to time/dose as long as there is an unlimited supply of oxygen in bulk lipids, their homogeneous solutions and microheterogeneous assemblies: fatty acids, monolayers, micelles, liposomes and membranes, as revealed by the literature. The addition of antioxidants to both autoxidizing and radiolyzing lipids in homogeneous and microheterogeneous phases results in the temporary inhibition of lipid oxidation (lag time/lag dose).

Natural lipid-containing materials often contain natural antioxidants which protect lipids. In the present work we describe radiation-induced hydroperoxidation of thin layers of lipids in natural and synthetic model systems, consisting of powders coated with oleic acid, with or without the addition of antioxidants. While the lag time in autoxidation could be extended by the addition of antioxidants, the lag dose in radiolysis could not be extended in the same way. The addition of antioxidants to irradiated systems only reduced the dose gradient of the post-lag oxidation. The lag dose appeared to be characteristic of the substrate and was not affected by the dose rate. At the same time, the amount of LOOH was inversely proportional to dose rate in both natural and synthetic model systems.

LIPID OXIDATION IN BILAYER LIPOSOMES INDUCED BY RADICALS FROM THE SURROUNDING WATER PHASES

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Some features of the radiation chemistry of organized assemblies were studied in aqueous dispersions of small unilamellar vesicles of egg yolk lecithin.

Free radicals were generated by irradiation in a gamma-radiation facility (PANORAMA/IOM, Leipzig) with doses up to 13 kGy, and by ns-pulse radiolysis using the pulse accelerator ELIT.

By means of ^{1}H-NMR spectroscopy (AM 250/BRUKER) the radiolytic degradation of some chemical groups of phospholipids in the irradiated samples were determined. Using the CARR-PURCELL-pulse sequence it was possible to obtain information about the radiation-induced restriction of the choline head group mobility for each individual lipid layer. By the same pulse sequence, some hydrophylic radiolytic products could be detected, which escape from the liposome into the water phase.

The concentration of the peroxides was determined by a sensitive iodometric method.

The radical attack on the bilayer was examined under different experimental conditions, including the addition of sodium azide or sodium chloride.

The yield $G = 3.8$ for the degradation of the allylic methylene group is smaller than published values for an equivalent homogeneous system. However, the conversion of OH radicals into N_3 radicals results in an enhancement of G by 35 %. This fact is an indication of a more specific attack of N_3 on the lipid core of the vesicle. In agreement with this interpretation, we have found a smaller restriction of the head group mobility in such samples which were irradiated in the presence of NaN_3.

By means of a competition experiment using p-nitroso-N,N-dimethylaniline a value of $k c_L = 5 \times 10^6$ s^{-1} was determined for the product of the rate constant k of OH radicals with lipid molecules and the concentration of lipids c_L (tot. lipid: 0.5 %). This value, which characterizes the attack of OH radicals on the lipid bilayer, is smaller by more than one order of magnitude in comparison with published data for homogeneous systems concerning the same radiosensitive fatty acid residues. From T_2-measurements of the outer and inner lipid head groups it could be deduced that the preferred site for radiation damage is the outer lipid layer. This may be a consequence of differences in radical fluxes from both water compartments towards the membrane.

The results confirm the hypothesis that the approach of radicals to the vesicle surface is a rate controlling feature in the process of lipid oxidation.

REACTIVITY OF IMIDAZOLES IN PULSE AND γ-IRRADIATED LIQUID AND FROZEN SYSTEMS

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The yields of decomposition and reactivities of imidazole as well as methyl, ethyl and propyl imidazoles have been studied in methanol and aqueous methanol solutions.

The yields of decomposition in liquid systems for all examined imidazoles are low and equal to 0,15 to 0,30 molecules per 100 eV.

It has been shown by pulse and γ-radiolysis that the above imidazoles are medium reactive towards electrons (second order rate constants near 10^8 M^{-1} s^{-1}). In the contrary, the reactivity of imidazoles towards oxidizing radicals are extremely low as it has been shown using pNDA as a competitive scavenger.

The above i. e. the medium reactivity of imidazoles towards the electrons and low reactivity towards oxidizing radicals have been supported in the frozen chloride-methanol glasses applying the spectrophotometric measurements.

On the Mechanism of the Electron-Initiated Curing of Acrylates

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Abstract - Using electron pulse radiolysis with optical detection the mechanism of the radiation induced polymerization of tripropyleneglycoldiacrylate (TPGDA) was studied in n-butylchloride (n-BuCl) solutions at room temperature. The dose per pulse was 50 or 130 Gy corresponding to the electron pulse lengths of 5 and 15 ns, respectively. Short- and long-lived transients, such as TPGDA radical cations and different types of radicals were observed.

The charge transfer from n-BuCl primary cations to the TPGDA solute is diffusion controlled with a rate constant of $k = 9 \times 10^9$ l·mol^{-1}·s^{-1}. The TPGDA cations produced undergo both rapid deprotonation and ion-molecule reactions with TPGDA. Deprotonation ($k \approx 3..5 \times 10^7$ s^{-1}) leads to TPGDA vinyl-type radicals. As products of the ion-molecule reactions two types of dimeric cations were observed: a covalently bonded dimer, and a charge resonance stabilized structure.

The covalently bonded dimer reacts with TPGDA ($k \approx 10^6$ l·mol^{-1}·s^{-1}) and forms a species in which excess charge and unpaired spin are separated by one molecular unit.

Addition of the vinyl-type radicals to TPGDA leads to the chain start of the radical polymerization. An upper bound of 10^5 l·mol^{-1}·s^{-1} was estimated for the starting reaction.

In the presence of oxygen the formation of vinyl peroxyl radicals is observed, and the polymerization is inhibited.

Semi-empirical quantum chemical calculations of electronic spectra performed for methyl acrylate cation and radical structures support the assignment of the various transient optical spectra to the species mentioned.

ESR STUDIES OF IRRADIATED POLYPROPYLENE AND ITS COPOLYMERS

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The following polymer materials: (i) isotactic polypropylene, (ii) low-density polyethylene, (iii) compositions of polypropylene and polyethylene with various content of polyethylene, and (iv) natural copolymers with the same composition, were irradiated and subsequently investigated using electron spin resonance technique.

Polymer samples have been irradiated by applying high-energy electrons from 13 MeV linear electron accelerator (LAE 13/9) over the dose range 10 - 40 kGy. For the sake of (i) controlling radiation degradation of polymers, (ii) radiation sterilization of medical equipment, and (iii) evaluation of radiation resistance of the investigated materials, the following dose ranges have been applied: 10 - 25 kGy, 20 - 35 kGy, and ~ 40 kGy, respectively.

The nature and the yield of primary radicals has been analyzed as a function of the absorbed dose and of the type of the polymer by means of EPR using a Bruker ESP-300 spectrometer. The yield of peroxyl radicals for various polymers and for their different composition has been also evaluated. On that basis, we are going to conclude about the mechanism of radiation-induced copolimerization of polymers in solid state.

ESR STUDY OF RADIATION INDUCED RADICALS IN POLYCRYSTALLINE METHIONINE AND ITS HOMOPEPTIDES

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The radicals formed on γ-radiolysis of L-methionine and its homopeptides (L-methionyl-L-methionine and L-methionyl-L-methionyl-L-methionine) in the polycrystalline state at 77 K and on subsequent warming over the temperature range 77-293 K are reported. For methionine and two homopeptides (L-Met-L-Met, L-Met-L-Met-L-Met) the radical species present at 77 - 95 K are the anion radicals formed by the addition of an electron to the carboxyl group (L-Met) or to the carbonyl oxygen of the peptide bond(s) (L-Met-L-Met and L-Met-L-Met-L-Met). On warming to 180 - 230 K, the deamination radicals which were previously observed in polycrystalline X-Met peptides, were not detected. Instead, only H-abstraction radicals in the side chain of methionine residue formed by the cationic pathway (when the sulphur-centred radical cation undergoes deprotonation at the α-position to sulphur atom) are observed. On further warming to 293 K, the recorded ESR spectrum indicates the presence of methyl radicals ($CH_3^·$) for L-Met and its homopeptides, and additionally of decarboxylation radicals for L-Met-L-Met and L-Met-L-Met-L-Met. The latter observation is consistent with the higher yields of CO_2 determined in γ-irradiated polycrystalline L-methionyl homopeptides using GC technique. The absence of deamination radicals accompanied by the presence of the relatively high yields of methyl radicals suggests that the cleavage of sulphur-carbon bond is the competitive process with the cleavage of nitrogen-carbon bond in the anionic pathway for methionine and its homopeptides.

NEW RADIATION DOSIMETRIC SYSTEMS BASED ON AMORPHOUS CHALCOGENIDE SEMICONDUCTORS

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Possibilities of practical application of amorphous chalcogenide semiconductors (AChS) as radiation-sensitive elements of solid state dosimetric systems are analyzed. In comparison with well-studied oxide glasses(1) these materials are characterized by less temperature threshold of radiation information bleaching (2).

Functioning technical principle of investigated dosimeters consists in rough monotonous dependence of spectral position of AChS optical absorption edge on ionizing radiation dose. Dosimetric characteristic of As_2S_3, As_2S_3-Sb_2S_3 and As_2S_3-Tl_2S vitreous and thin films samples in the case of gamma-irradiation with Co^{60} radioisotope source (E = 1.25 MeV) and accelerated electrons irradiation with energy 1 - 3 MeV are considered. Post-radiation effects in irradiated AChS of various chemical composition are studied.

Physical principles of functioning of AChS based dosimetric systems are radiation-stimulated of co-ordination defects formation, switching and annihilation caused by disturbance of intramolecular covalent bonds balance (3). Nature of these processes are studied using differential Fourier spectrometry technique in 400 - 100 cm^{-1} region.

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INFLUENCE OF ELECTRICAL FIELD AND DOSE RATE ON RADIATION CURING OF UNSATURATED POLYESTER RESINS

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The course of radiation curing of unsaturated polyester resins was followed by electrical conductivity change. Both the electrical field strength and dose rate influenced the crosslinking. The electrical field somewhat increased the reaction rate possibly due to the orientation in a polar system. To investigate the effect of electrical field, the samples were irradiated to different doses at different field strengths. The electrical fields under the consideration ranged from 2.5 kV/m to 250 kV/m. The results of the extraction analysis of irradiated samples confirmed the influence of the electrical field.

The electrical field effect depended on the dose rate. Three dose rates were applied: 3,05 kGy/h, 0,354 kGy/h and 0.096 kGy/h. The medium dose rate gave the highest reaction rate (on dose scale). On basis of the obtained results, the electrical field and dose rate effects could not be simply explained. Both the orientation of sample molecules and changes of reaction mechanism could occur.

OXIDATiON OF AMMONIA IN MOIST AIR BY USE OF PULSE CORONA DISCHARGE TECHNIQUE

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Experiments by pulse corona discharge (PCD) induced gas-phase oxidation of NH_3 (concentrations 5×10^{-3} - 5 vol.%) in moist air (~ 2 vol.% H_2O) at room temperature has been studied.

High voltage generator enables generation of DC-voltage up to 35 KV and pulse voltage with duration 150-350 ns up to 100 KV and frequencies $2\text{-}100 \ s^{-1}$.

Stainless-steel reactor chamber in the form of cylinder with diameter 60 mm together with UV-source (mercury lamp of middle pressure) with coaxial system of coronating electrodes (stainless steel, Pt, etc.) has been used.

It has been shown that in static and flow conditions (flow rate 0,3-10 l/min) oxidation of NH_3 took place with production of N_2 or NH_4NO_3 The probability of these channels depends on material and shape of coronating electrodes.

The rate of NH_3 decay is proportional of DC-and PCD-current. In the aosence of NH_3 increasing of O_3 concentration considerably decreases of DC-and PCD-current values.

Combination of PCD and UV-irradiation considerably (2-5 times) increases the efficiency of NH_3 removal. By UV irradiation O_3 decays by light:

$$O_3 + h\upsilon(254 \ nm) \rightarrow O \ (^1D) + O_2$$
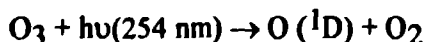
Very active singlet oxygen atoms reacts with water vapours:

$$O(^1D) + H_2O \ \text{---} \ OH + OH \qquad K_{298} = 3.5 \times 10^{-10} \ cm^3 s^{-1}$$

with production of OH - radicals.

The mechanism of PCD-and UV induced oxidation NH_3 in gas phase has been considered. The role of different intermediates (oxygen atoms, OH, NH_2 radicals, etc.) has been analyzed.

Studies on Photofading and Stable Free Radical Formation in Reactive Dyed Cellulosic Systems under their Exposure to Light.

Edit Rémi*, Olga Horváth*, András Víg*, Antal Rockenbauer,
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Abstract

The formation of stable free radicals could be detected earlier in the course of exposure to light of reactive dyed cotton fabrics.

To obtain more detailed information the changes of the stable free radicals were measured in function of the wavelength of light on azo-reactive dyed cotton fabrics and cellophane films.

Samples were exposured to light in a device named Spectrotest (Original Hanau). Photofading was followed on cotton fabrics by means of measuring of colour difference and on cellophane films by measuring changes in optical density. Correlation was sought for between the kinetics of photofading and that of stable free radical formation. Under exposure to low energy light photofading slowed down significantly while the formation of stable free radicals remained well detectable.

It could be assumed that photofading was preceded by the formation of stable free radicals.

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Mrs. Lóki, Mária

	Sunday, Sept 4	Monday, Sept 5	Tuesday, Sept 6	Wednesday, Sept 7	Thursday, Sept 8
9	OPENING	*SESSION 4* POLYMER, RADIATION, I	*SESSION 8* POLYMER, UV	*SESSION 10* HYDROCARBONS	*SESSION 14* ORG., COMPLEX
10			*SESSION 9* POSTER		
11	*SESSION 1* INTRODUCTION, GENERAL				CLOSING
12		*SESSION 5* POLYMER, RADIATION, II	LUNCH	*SESSION 11* DOSIMETRY	LUNCH
13	LUNCH	LUNCH		LUNCH	
14	*SESSION 2* INTRODUCTION, POLYMER	*SESSION 6* BIOLOGY, I	EXCURSION	*SESSION 12* AQUEOUS, I	
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16			CONFERENCE DINNER	*SESSION 13*	
17	*SESSION 3* INTRODUCTION, AQUEOUS	*SESSION 7* BIOLOGY, II		AQUEOUS, II	
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