

FINAL REPORT

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Hazardous Gas Production by Alpha Particles
in Solid Organic Transuranic Waste Materials

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Executive Summary

This project focused on the production of hazardous gases in the radiolysis of solid organic matrices, such as polymers and resins, that may be associated with transuranic waste material. Self-radiolysis of radioactive waste is a serious environmental problem because it can lead to a change in the composition of the materials in storage containers and possibly jeopardize their integrity. Experimental determination of gaseous yields is of immediate practical importance in the engineering and maintenance of containers for waste materials. Fundamental knowledge on the radiation chemical processes occurring in these systems allows one to predict outcomes in materials or mixtures not specifically examined, which is a great aid in the management of the variety of waste materials currently overseen by Environmental Management.

This project was successful in designing several novel devices for heavy ion radiolysis and applying them to the measurement of gaseous products in a variety of polymer materials commonly associated with radioactive waste. Gas production was determined in the radiolysis with gamma rays, protons, helium ions, and carbon ions. These particles are representative of the different radiation fields that might be experienced in mixed waste storage environments, such as neutrons, alpha particles, and heavy recoil ions. Hydrogen is the most common hazardous gaseous product, although methane and ethane are possible, depending on the particular material. The yields of hydrogen were found to increase by an order of magnitude from gamma ray to alpha particle radiolysis in some polymers. This project made an important step toward having the ability to quantitatively estimate the radiolytic response to specific radiation and to

predict variations in product yields within a class of polymers. This type of capability will be vital in order to elucidate polymer degradation in storage environments containing complex mixtures of transuranic waste.

The polymers examined in this project include polyethylene, polypropylene, poly(methyl methacrylate), polystyrene, polyisobutylene, poly(4-vinylpyridine), and several types of nylons. The systematic examination of these of polymers made it possible to form preliminary models of the basic mechanisms leading to the experimental observations. Because of versatility of the experimental techniques developed in this project, gaseous product yields and their diffusion through the polymers could be examined. Diffusion processes are important in understanding delayed radiation effects involving long-lived reactive species and for predicting gas migration from bulk polymers or between membranes. The knowledge obtained from the work performed in this project will make a substantial contribution toward the long-term management of gas production in transuranic and other mixed waste materials.

The fundamental experimental approach of this project allows the results to be compared with the large amount of basic radiation chemistry studies on liquid organic materials. However, much of the work can be immediately applied to practical situations. The results of this project will make it easier to predict accurate rates of gas buildup in storage containers containing mixed transuranic waste and help in the engineering of future storage and transport containers. All of the data obtained in this project will be published in the open literature to ensure availability to everyone.

Research Objectives

The management and disposal of mixed waste containing transuranic radionuclides is a major activity of the Department of Energy. [1] These radionuclides, plutonium, americium, neptunium, etc., are alpha particle emitters and the energy deposited by the alpha particles is causing chemical transformations in the matrices accompanying the waste. It is important for the success of the Environmental Management Science Program to be able to predict the effects of radiation induced chemical transformations on the local environment of the waste. Of particular concern is the radiolytic generation of gases such as hydrogen, which may pose flammability or explosive hazards. Information on the basic radiation chemical mechanisms responsible for production of these gases from solid organic matrices is scarce. Progress has been made in understanding the radiolysis of the aqueous phases and other structural elements associated with the storage of radioactive waste. [2] Many more studies in this field are currently underway. The fundamental processes occurring in solid hydrocarbon matrices such as polymers and resins are just beginning to be understood. These matrices are associated with many of the transuranic waste deposits or the transportation of these radionuclides and they represent a significant Environmental Management problem.

Basic radiation chemical studies of solid polymers initiated by conventional radiation such as γ rays or fast electrons have been performed. [3] However, very little is known about the radiation chemical decomposition mechanisms of these compounds when the irradiating particle is a heavy ion such as an alpha particle. Without specific knowledge of the chemical transformations occurring, it is very difficult to predict how the local environment around the radioactive waste is changing with time. Some of the

products being formed are likely to lead to special maintenance or transportation problems. For example, similar problems in closed aqueous systems required extensive engineering efforts in the cleanup of Three Mile Island. [4] This project has measured the yields of hydrogen, methane, and ethane, in a number of polymers that present a significant immediate hazard in the self-radiolysis of transuranic waste deposits.

The successful management of transuranic wastes requires fundamental radiation chemical studies with heavy ions because their radiolysis is very different than that found with the more commonly used γ rays. The inadequacy in basic knowledge may lead to serious problems for Environmental Management. Experiments with heavy ions such as protons and helium ions are not common because of the lack of suitable expertise and appropriate resources. Only a few accelerator facilities have been modified to perform radiation chemical studies and virtually none of these are used routinely. Heavy-ion radiation chemistry has been regularly examined at the University of Notre Dame for many years, which greatly increased the probability of a successful completion of this project. The practical applications of this research are as important as the fundamental scientific knowledge on radiation degradation. Basic scientific information makes it easier to construct models of radiation damage to polymers and to compare the results with other radiation chemical studies on liquid hydrocarbons, for which there are considerably more experimental results. [5-13] Similarities in the radiolysis mechanisms of solid and liquid organic systems tie the work of this project with the broader field of liquid phase radiation chemistry.

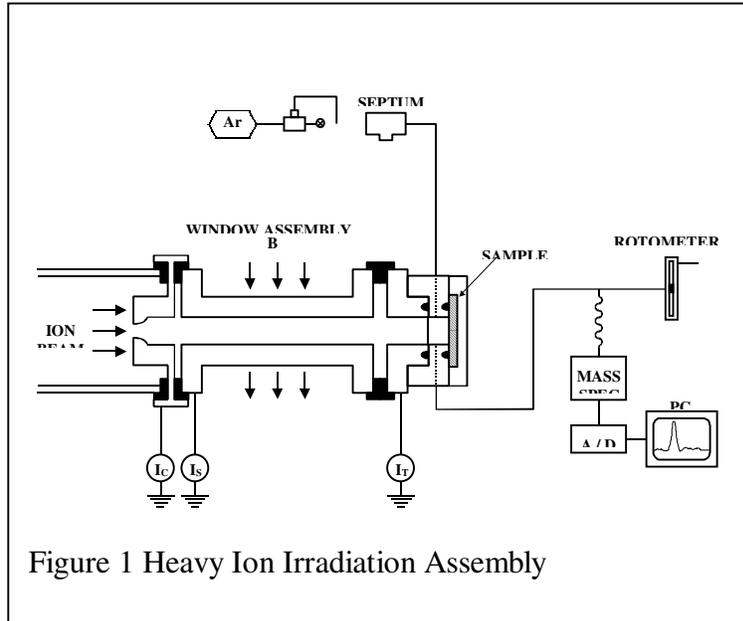
Methods and Results

Materials: A variety of solid polymers were used in the present study. They include low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), poly(methyl methacrylate) (PMMA), polyisobutylene (PIB) poly(4-vinylpyridine) (PVPy), polyamides (Nylon 12, Nylon 11, Nylon 6/12, Nylon 6/9, Nylon 6/6, and Nylon 6), and poly(dimethyl acid-co-alkyl polyamine) (PDAPA). The samples were obtained from Aldrich and GoodFellow and were of the highest quality except for LDPE, which was a commercial grade. Some of the samples were chopped, shaved into coils or pressed into thinner sheets from the original stock. All polymers were cleaned by rinsing in distilled water several times and dried in a vacuum oven for 3-5 hours.

Irradiations: A Shepherd Co-60 source was used for the γ radiolysis experiments. The dosimetry was determined by using Fricke dosimeter as described previously. [14] Electron density normalization was used to convert to the equivalent dose for the different polymers. The polymer samples were loaded into a quartz cell (2 cm in diameter and 4.5 cm tall) and inserted into the radiation zone of the cobalt source to be irradiated for fixed times. The cell had an inlet and exit port through which a carrier gas could be used to purge the sample.

Heavy ion irradiations were performed using 2-15 MeV ^1H ions, 5-20 MeV ^4He ions, and 10-30 MeV ^{12}C ions obtained from the 10 MeV FN Tandem Van de Graaff accelerator of the University of Notre Dame Nuclear Structure Laboratory (funded by the U. S. National Science Foundation). The window assembly is illustrated in Figure 1. The

accelerated ions passed successively through a collimator, a magnetic electron suppression tube, a vacuum exit window, the carrier gas for collecting the sample, and finally the solid polymer target. The polymer targets were about



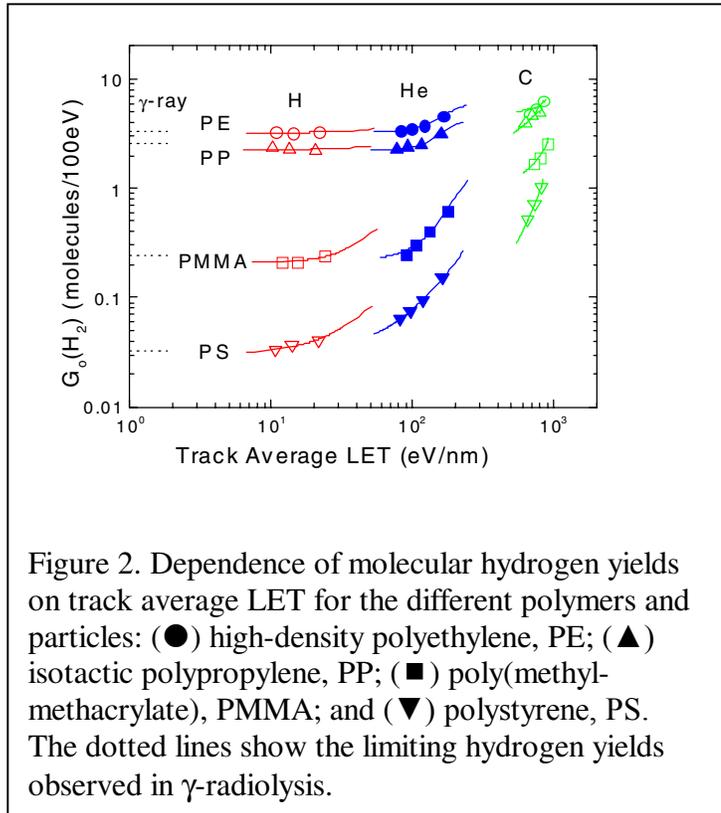
3 mm thick, which was sufficient to stop the ions (range of about 0.1 mm in HDPE for 10 MeV ^4He ions) and allow the gases of interest to diffuse mainly back into the carrier gas. Incident ion energy was determined by magnetic analysis, and energy loss to the windows was calculated using standard stopping power tables. [15] The end window and sample holder are essentially a Faraday cage. Absolute dosimetry was obtained by collecting and integrating the charge from the end window and sample cell in combination with the particle energy. Beam currents were about 5 ~ 15 nA, which was sufficient to obtain a large response of the gas signals. The total energy deposited was (5 ~ 15) $\times 10^{18}$ eV given within about 10 ~ 50 seconds. The beam diameter was 6.35 mm, and completely stripped ions were used, so the particle flux was about (1 ~ 15) $\times 10^{11}/Q$ particle/($\text{cm}^2 \text{ s}$)

Gas Analysis: In both γ and heavy ion radiolysis, UHP grade argon gas was used as the carrier gas to flush through the quartz cell (in the case of γ radiolysis) or through the void

between the exit window and the polymer disk (in the case of heavy ion radiolysis). The effluent of the carrier gas was normally monitored throughout the radiolysis using an inline technique. A quadrupole mass spectrometer (Balzers, QMA140 analyzer with axially mounted SEM) was used to monitor the gas products downstream from the radiolysis cell through a capillary tube ($\phi = 50 \mu\text{m}$, $l = 20 \text{ cm}$). A multiple-ion-detection mode was used in those cases of more than one gaseous product. The dwell time for each mass channel was set to 50 ms and the time needed to shift between the channels is limited by the mass spectrometer hardware, which was found to be not larger than 50 ms. Thus even 4 to 5 gases could be monitored simultaneously, and the time to collect the data from all the channels is not longer than 0.5 second. Calibration was conducted by syringe injection of high purity gases into the carrier gas stream. The dependence of the intensity on the gas volume normally exhibited a good linear relationship. All the experiments were carried out in room temperature at about 24 °C.

Some product yields were extremely low and could not be detected without first collecting the gases. In these instances, a four-way valve was used to isolate the sample from the argon carrier gas. The sample was first purged of air and then isolated throughout the radiolysis. After a given dose, the valve was opened to allow the carrier gas to flush the sample cell. This technique also worked well for those gases that diffused slowly from the polymer bulk. In these studies, the sample cell was isolated for varying periods of time following a fixed radiolysis interval (equivalent dose). Sampling the gaseous yield in this manner gave good estimates of gas diffusion rates from the bulk polymer.

Results: Radiation chemical yields are typically given in units of molecules/100 eV of total energy adsorbed. The track structure largely determines the radiation chemical yield. No single parameter, such as energy, velocity, etc., determines the radiation track structure, but the linear energy transfer, LET (= dE/dx , the stopping power) is commonly used to represent the



general track structure. The radiation chemical yields of H_2 from polyethylene, polypropylene, poly(methyl methacrylate), and polystyrene are shown in Figure 2 as a function of the track averaged LET for various types of radiation. It can be seen that H_2 yields are very dependent on the type of polymer. The γ radiolysis H_2 yields with polystyrene are more than two orders of magnitude less than found with polyethylene. It is unclear if the decomposition of polystyrene is more radiation resistant than polyethylene or if it gives small H_2 yields because of the chemistry. This difference is very important and further work should be performed. All H_2 yields increase with increasing LET. Increasing the LET increases the concentration of reactive species, and thereby second order reactions, in the particle track. The increase in yields with polyethylene is about 40% for 5 MeV 4He ions and 100% for 10 MeV ^{12}C ions from that

observed with γ rays. For polystyrene, the increase is about 450% for 5 MeV ^4He ions and 3000% for 10 MeV ^{12}C ions from that observed with γ rays. Clearly, the radiation chemical yield of H_2 is very dependent of the type of particle and its energy. It appears that all H_2 yields are approaching a common value at very high LET. This result suggests a common precursor and further studies should be performed to examine the processes involved.

Nylons are polyamides with varying numbers of methylene groups between the amides. Since it is believed that most H_2 formation first involves carbon – hydrogen bond breakage, the nylons offer a good opportunity to examine the effect of carbon – hydrogen bond density on H_2 yields within a given class of polymers. Figure 3

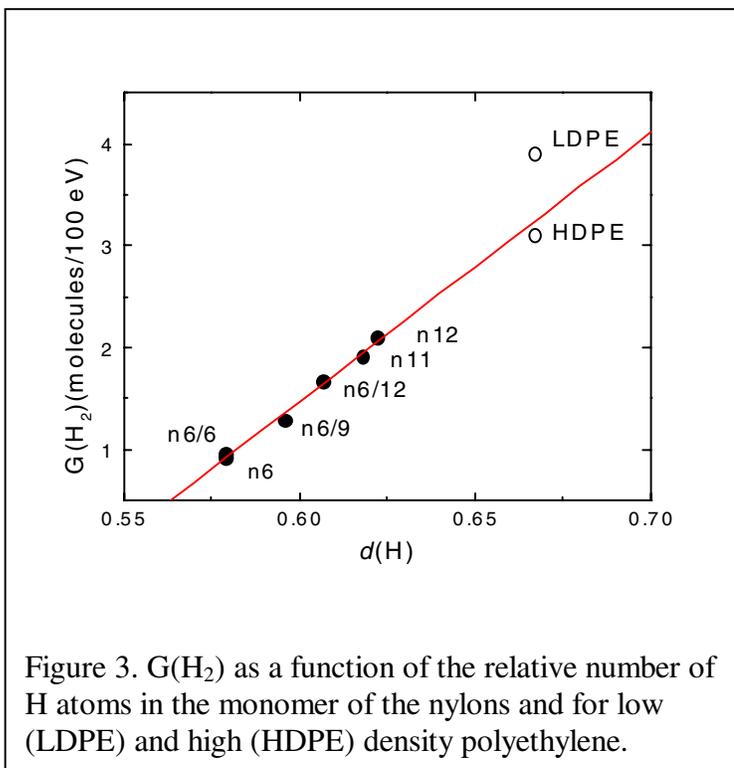


Figure 3. $G(\text{H}_2)$ as a function of the relative number of H atoms in the monomer of the nylons and for low (LDPE) and high (HDPE) density polyethylene.

shows the H_2 yields for various nylons as a function of the relative number of H atoms in the monomer unit, $d(\text{H})$ (i.e. the ratio of the number of H atoms to the number of all the atoms in the monomer unit). It can be seen that density of H atoms is a good predictor of H_2 yields within a given class of polymers. However, the result is not universal for all polymers, for instance the results with nylons do not predict accurate H_2 yields with

polyethylene or polystyrene. Considerable more work is required to understand the effects of side chain groups, crystallinity, etc. on H₂ yields.

It was soon discovered in the course of this project that diffusion of the gases from the bulk polymer is very important in their measurement. Some of the differences in yields in the literature can be due to incomplete collection of the gases. A few effects ascribed to temperature are due to diffusion and not chemistry. The online technique used in these experiments can be used to obtain diffusion coefficients. Several

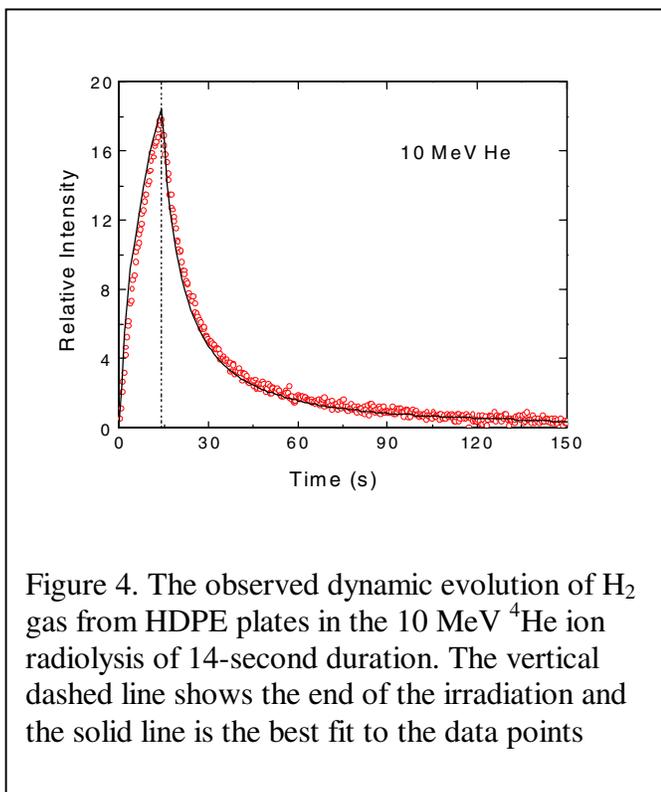


Figure 4. The observed dynamic evolution of H₂ gas from HDPE plates in the 10 MeV ⁴He ion radiolysis of 14-second duration. The vertical dashed line shows the end of the irradiation and the solid line is the best fit to the data points

different diffusion models were developed to match the irradiation geometry and the observed gas evolution profiles were fit with the models to give best estimates of yields and diffusion coefficients. Figure 4 shows a typical H₂ evolution curve for a 10 MeV ⁴He ion in polyethylene and the fit of the model simulation to the data. A large number of diffusion coefficients and yields were determined from the simulations to the data. Table I gives some of the results for the γ radiolysis of various polymers. Similar studies were also performed with alpha particles.

Table I. Diffusion coefficients and G-values in the γ -radiolysis of polymers.

Polymer Sample	Gas Species	<i>D (sim.)</i> (10⁻⁶ cm²/s)	<i>G (sim.)</i> (molec./100 eV)	<i>G (exp.)</i> (molec./100 eV)
LDPE	H ₂	3.5	3.82	3.9
	CH ₄	0.0098	0.13	0.6
HDPE	H ₂	2.2	3.25	3.3
PP	H ₂	6.5	2.7	2.6
	CH ₄	0.12	0.054	0.083
PS	H ₂	4.4	0.039	0.033
PMMA	H ₂	0.89	0.24	0.24
	CH ₄	0.065	0.031	0.033
	CO ₂	0.27	0.27	0.29
Nylon11	H ₂	0.74	1.87	1.92
Nylon 6	H ₂	0.69	0.92	0.98
PDAPA	H ₂	0.61	1.3	1.5

The simulated diffusion coefficients agree well with the few values in the literature and significantly increase the ability to predict gas migration from bulk materials or through membranes. This work is also useful for examining latent effects due to long-lived radicals or other reactive species. For instance, carbon dioxide formation in nylon may be due to the decomposition of a relatively long-lived excited species. Further models should include both diffusion and reaction in order to better understand polymer degradation and gas formation by the different types of radiation.

Relevance, Impact, and Technology Transfer

The following points specifically address the relevance, impact, and technology transfer of this project in the context of the Environmental Management Science Program.

- a. This project focused on the hazardous gas production in the self-radiolysis of transuranic waste containing solid organic polymers and resins. Yields of H₂, methane, and ethane were determined for a wide variety of polymers with different types of radiation. The results with helium ions are especially important because they mimic radiation damage due to the alpha particles in transuranic mixed waste environments.
- b. The results of this project will make it easier to predict gas buildup in storage containers containing mixed transuranic waste and help in the engineering of future storage and transport containers.
- c. The experimental approach in this project has been from a fundamental basis so that the results could be compared with the large amount of basic radiation chemistry studies on liquid organic materials. The work spans the range from fundamental science examining the underlying mechanisms for radiolytic decomposition to practical results that can be applied immediately.
- d. The results of this work will be used by anyone wishing to determine the extent of hazardous gas formation from transuranic waste mixed with solid organic materials and by basic scientists working on fundamental radiolytic

decomposition mechanisms of polymers. Not many projects have this broad range of applicability.

- e. This project has given DOE an unusual capacity to examine the radiolytic decomposition of solid organic materials by heavy charged ions. Very few facilities in the world are capable of performing these experiments and no facility combines the resources and expertise that was applied to this project.
- f. Most of the current investigations on the radiolysis of polymers involve the use of γ rays or high-energy photons. This project has strengthened the ties between the principal investigator and several other worldwide groups working on general polymer radiolysis. It is expected that these ties will lead to significant advances in understanding the fundamental radiation science of polymers.
- g. The research obtained in this project has led to new insights on the fundamental decomposition of solid organic materials leading to H₂ formation. Commonalities between different polymers and between solids and liquids have been discovered that will greatly aid in the future probing of decomposition mechanisms. These discoveries are directly due to the responses of the materials to the different types of incident radiation.
- h. The results of this project can be directly applied to many current DOE Environmental Management problems. However, more fundamental information on different classes of polymers and their mixtures is required to estimate radiolytic response of unexamined systems.
- i. All of the data obtained in this project will be published in the open literature. No contact has been made to examine a specific environmental condition.

Project Productivity

The project was successful in examining the H₂ production in a wide variety of polymeric materials. All of the proposed goals were met or exceeded and the results can be immediately applied toward DOE Environmental Management problems. Several unexpected results such as obtaining gas diffusion coefficients were a surprise and may prove to be quite useful. However, more work in this field is required before the fundamentals of gas production are understood. Only then will one be able to predict radiolytic decomposition in unexamined systems or in complex mixtures.

Personnel Supported

Faculty:	Dr. Jay A. LaVerne supported at 4 months per year for 3 years
Post-doc:	Dr. Zheng Chang supported at 12 months per year for 3 years
Undergraduate student:	Mr. Kevin Hadley supported for 3 months

Publications

Z. Chang and J.A. LaVerne, "Molecular Hydrogen Production in the Radiolysis of High-Density Polyethylene" **J. Phys. Chem. B** 1999, **103**, 8267.

Abstract: The production of molecular hydrogen in the radiolysis of high density polyethylene by γ rays and heavy ion beams has been investigated. Only the slightest increase in the radiation chemical yield of 3.1 molecules/100 eV was found from γ rays to protons of 5 – 15 MeV. A gradual increase in yield was observed on further increasing the linear energy transfer of the incident particles. This increase amounted to almost a doubling in the hydrogen yield from 10 eV/nm protons to about 800 eV/nm carbon ions. The exact reason for the increase in molecular hydrogen yield is uncertain, but it may involve reactions of excited states or enhanced combination reactions of carbon centered radicals thereby allowing more hydrogen to escape the particle tracks. Diffusion from the bulk material was found to have a dominant role on the observed dynamic profiles of hydrogen gas. A simple one-dimensional diffusion model was used to estimate the diffusion constant of hydrogen in polyethylene to be 2.2×10^{-6} cm²/s.

Z. Chang and J.A. LaVerne, "Hydrogen Production in γ -Ray and Helium-Ion Radiolysis of Polyethylene, Polypropylene, Poly(methyl-methacrylate), and Polystyrene" **J. Poly. Science, Part A, Polymer Chemistry**, 2000, **38**, 1656.

Abstract: The production of molecular hydrogen in the radiolysis of high-density polyethylene, isotactic polypropylene, poly(methyl methacrylate), and polystyrene by γ -rays and 5-20 MeV helium ions has been investigated. Molecular hydrogen is the dominant gaseous product from these polymers and the yields with γ -rays are 3.3, 2.6, 0.24, and 0.033 molecules/100 eV of energy absorbed for polyethylene, polypropylene, poly(methyl-methacrylate) and polystyrene, respectively. The decrease in observed hydrogen is due to increased branching and the chemical nature of the groups on the side-chains. There is an increase in hydrogen production on increasing the linear energy transfer (LET) from γ -rays to helium ions, but the relative increase depends on polymer type. With incident 5 MeV helium ions the respective yields of molecular hydrogen are 4.6, 3.2, 0.62, and 0.15 molecules/100 eV. The increase in molecular hydrogen with increasing LET may be due to changes in the kinetics of hydrogen precursors in the particle tracks. The differences in the relative increases in molecular hydrogen with increasing LET for each of the polymers suggests that self-scavenging reactions may be important for low LET particles.

Z. Chang and J.A. LaVerne, "Hydrogen Production in the Heavy Ion Radiolysis of Polymers. 1. Polyethylene, Polypropylene, Poly(methyl-methacrylate), and Polystyrene"

J. Phys. Chem. B, 2000, **104**, 10557.

Abstract: The production of molecular hydrogen in the radiolysis of isotactic polypropylene (PP), poly(methyl-methacrylate) (PMMA) and polystyrene (PS) with protons and carbon ions has been investigated. Previous experimental data on the above polymers with γ -ray and helium ion irradiations have been combined with similar studies on high-density polyethylene (PE) to give a comprehensive survey of the dependence of molecular hydrogen yields on particle linear energy transfer, LET, in the range of 0.2 eV/nm to 800 eV/nm. The radiation chemical yields of molecular hydrogen are very dependent on LET and generally increase with increasing LET. However, the relative change in hydrogen yield as a function of LET is very different for the various polymers. It appears that with increasing high LET the hydrogen yields for each of the polymers are approaching the same value. This observation suggests that the radiolytic source of molecular hydrogen is similar for all of the polymers and increases with increasing LET of the irradiation. Unexpectedly high yields of molecular hydrogen can have implications in many fields including those that involve heavy charged particles and intense photon sources.

Z. Chang, J.A. LaVerne, "Dynamic Evolution of Gases in the γ - and Helium-Ion Radiolysis of Solid Polymers" **J. Poly. Science, Part B, Polymer Physics**, 2001, **39**,

1449.

Abstract: The dynamic evolution of gaseous hydrogen, methane and carbon dioxide in the γ - and ^4He ion radiolysis of solid polymers was investigated. The polymers used include low-density and high-density polyethylene, polypropylene, polystyrene, poly(methyl methacrylate), Nylon 11, Nylon 6 and poly(dimmer acid-co-alkyl polyamine). An inline quadrupole mass spectrometer was employed to monitor the dynamic profiles of the gases produced in the radiolysis. One- and two-dimensional numerical diffusion models were developed to simulate and extract optimum diffusion coefficients and gas yields from the experimental dynamic gas profiles. It was found that the dynamic evolution of molecular hydrogen from the bulk polymer is controlled by its diffusion in most cases as is the case for CO_2 in poly(methyl methacrylate). In the γ -radiolysis of some polymers such as low-density polyethylene and polypropylene, the dynamic evolution of methane is only partially controlled by the diffusion process and some other post-irradiation process is a factor. It is concluded that the simulation method developed in the present paper is helpful in understanding and predicting the mechanisms of the gas evolution in the radiolysis of solid polymers

Z. Chang and J. A. LaVerne, "The Gases Produced in Gamma and Heavy-Ion Radiolysis of Poly(methyl methacrylate)" **Radiat. Phys. Chem.** 2001, **62**, 19.

Abstract: The production of CO, CO₂, H₂ and CH₄ gases in the γ -radiolysis and heavy-ion radiolysis of poly(methyl methacrylate) was investigated. It was found that the dynamic evolution of the radiolytic gases from the polymer surface is controlled by molecular diffusion in the polymer matrix. Diffusion coefficients were extracted by model fits to the observed temporal profiles. The gas yields were determined as a function of the linear energy transfer, LET, in the range of 0.2 to 830 eV/nm. It was found that for heavy-ion irradiations the total gas yield increases significantly when the LET increases above 80 eV/nm. The results clearly show that the degradation mechanisms of PMMA are affected by LET. It appears that H₂ and CH₄ are formed from precursors different than those leading to CO and CO₂. The LET dependence suggests that the latter two products are not completely formed from a common precursor, which has been previously proposed.

J. A. LaVerne, Z. Chang and M. S. Araos "Heavy Ion Radiolysis of Organic Materials"

Radiat. Phys. Chem. 2001, **60**, 253.

Abstract: Radiation chemical processes induced by the passage of heavy charged particles in organic materials are discussed. An overview of the physics of energy loss processes on the subsequent chemical reactions is given. The effects of the dominant physical parameter, the linear energy transfer, LET, on the radical and molecular products from organic compounds are examined. It is shown how the complex interaction of excited states and radical intermediates can sometimes make it difficult to predict the variation of final product yields with high LET radiation. Molecular hydrogen yields are examined in detail because of their fundamental and practical aspects. Hydrogen formation is especially interesting because it is produced by a variety of reactions with different relative LET dependences. The yield of H₂ is found to be very similar for liquid organic molecules and solid polymers containing the same molecule as the side group connected to the main carbon - carbon backbone. Biradical products and cross-linking yields are also found to be comparable suggesting very similar chemistry between the liquid and solid compounds.

Z. Chang and J. A. LaVerne, "The γ Radiolysis of Nylons: Molecular Rearrangement and Gas Production" **J. Phys. Chem. B.** in press.

Abstract: The γ radiolysis of nylons 12, 11, 6/12, 6/9, 6/6 and 6 were investigated. The IR spectra of film samples before and after the γ -radiation show the formation of amines, aldehydes, and ketones, and suggest that the cleavage of amide group is one of the major processes of radiolysis. The yields of gaseous products and their evolution from the bulk were measured with a quadrupole mass spectrometer. Four gases were determined as the

major radiolytic products and their yields were found to be in the order $H_2 > CO > CO_2 > CH_4$ for all the nylons. The relationship between the gas yields and the chemical composition of the monomer unit shows that the H_2 yield increases with the relative number of H atoms. The results suggest a random distribution of energy leading to H_2 production. It was found that the yields of CO and CO_2 decrease with an increase in the relative number of amide groups on the nylon monomer unit. Since these later products must be derived from the amide group, chain scission and fragmentation at the amide group must decrease with increasing amide contribution to the monomer unit of the polymer chain. The diffusion coefficients of H_2 , CO and CO_2 gases in the bulk polymer were determined and the results suggest that post-radiation processes exist in the γ radiolysis of nylons.

Z. Chang and J. A. LaVerne, "The Gamma and Heavy-Ion Radiolysis of Polyolefins" in preparation.

Abstract: The γ - and heavy-ion radiolysis of polyethylene was investigated with various techniques in this paper. The radiation yields of many chemical products including hydrogen and methane gases, crosslinking and chain scission, and unsaturated bonds were observed in the irradiations with γ -rays, proton, helium and carbon ion particles. The yield of H_2 gas produced in the γ - and helium ion radiolysis of polyethylene was also measured with high irradiation doses. According to the experimental results, it was found that the efficiency of radiolysis of polyethylene is increased with increasing the particle linear energy transfer (LET) of irradiation. The LET dependences of the yields of the chemical changes were also compared with the corresponding radiation temperature dependences. It was found that the LET effects are rather similar to the temperature effects on the radiation yields; there are no new radiolytical products in remarkable amount observed by either increasing radiation temperature or particle LET. This finding may be helpful in further understanding the radiation chemistry in the heavy-ion radiolysis of polyethylene.

Interactions

Presentations: Poster

Jay A. LaVerne, "Hydrogen Production in the Radiolysis of Polymers" 218th American Chemical Society National Meeting, New Orleans, LA August 21-25, 1999.

Z. Chang, "Production of Hydrogen Gas in the Heavy-Ion Radiolysis of High-Density Polyethylene" 218th American Chemical Society National Meeting, New Orleans, LA August 21-25, 1999.

Jay A. LaVerne and Z. Chang, "Production of Hydrogen in the Heavy Ion Radiolysis of Polymers", Gordon Conference on Radiation Chemistry, Plymouth, NH, June 25-30, 2000.

Presentations: Invited Talks

Jay A. LaVerne, "Heavy Ion Radiolysis of Organic Materials", International Symposium on Prospects for Application of Radiation towards the 21st Century, Waseda University, Waseda, Japan, March 14, 2000.

Jay A. LaVerne, "Production of Hydrogen in the Heavy Ion Radiolysis of Polymers", EMSP National Workshop, Atlanta, Georgia, April 26, 2000.

Transitions

The information obtained from this project has been published in the open literature so that it is readily available. Several inquiries suggest that the data is being used, but no specific case of the transition of the knowledge obtained in this project to any federal agency or industry is known.

Patents

No patents have been obtained from the work of this project.

Future Work

A considerable amount of work can still be done in the field of polymer radiolysis that would be of great use to the storage and management of mixed waste materials. This project examined many of the polymers with a backbone made up of carbon atoms and many of the nylons (polyamides). However due to time limitations, many other polymers with similar structures were not examined and other entire classes of polymers have not been explored, for instance polysilanes and some resins. Gas production and diffusion were the main thrusts of the research, but other aspects of polymer radiolysis are important for determining the underlying mechanisms. For instance, bond breakage and chain scission studies will give information on the mechanical stability of the residual polymer following radiolysis. These studies will help elucidate the mechanisms of

polymer decomposition and greatly aid in the ability to predict the response of systems not yet or unable to be examined experimentally. It is impossible to examine all polymers and knowledge of the mechanism allows one to construct models to help predict radiolytic decomposition. Although this project made a significant advance in the collection of more data in this field, the work is still too sparse to be able to construct the detailed models that will be required to predict the radiolytic response to many of the complex mixtures encountered by Environmental Management.

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