

Hydrogen Production in the Heavy Ion Radiolysis of Polymers. 1. Polyethylene, Polypropylene, Poly(methyl methacrylate), and Polystyrene

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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 0.2–800 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.

Introduction

The production of gases is an important and obvious chemical outcome in the radiolysis of solid polymers.^{1,2} Unlike other heavier components produced in the radiolysis, gases can usually diffuse out of the bulk material and be readily observed without further processing of the irradiated polymer. Among all the gaseous products, molecular hydrogen perhaps is the most important and predominant product in polymer radiation chemistry.² Carbon–hydrogen bonds are readily broken in radiolysis and much of the subsequent chemistry (e.g., cross-linking, combination, abstraction, and disproportionation) is due to the carbon centered radical and the H atom produced in this process.³ In many cases the H atom will predominantly undergo hydrogen abstraction reactions with the medium and the yield of hydrogen gas can be used as an indicator to evaluate the total carbon–hydrogen bond breakage in the polymer. Hydrogen production in polymers is perhaps the most sensitive indicator of the overall radiolytic decomposition.

There are very few ways to modify the composition of a bulk polymer in order to elucidate the radiolytic decomposition. A number of scavengers have been added to molten polyethylene in order to probe specific chemical processes.⁴ Chromophores have been added to polymer films to examine singlet excitation processes.⁵ Another technique for exploring reaction mechanisms is the variation in the type of radiation. Different types of ionizing radiation can have very different track structures in passing through matter because of the variation in rates of linear energy transfer, LET (equal to the stopping power, $-dE/dx$).⁶ The track structure affects the initial concentrations of reactive species and thereby modifies the rates of second order reactions. Products formed mainly through second-order processes can show a profound dependence on particle type. In recent years, some of the effects of energy deposition density on the chemical products have been examined in solid polymers.^{7–16} Foti and his colleagues^{7,8} investigated the cross-linking of polystyrene

and found that it increases with particle LET. Lee and co-workers^{9–12} studied the yields of gas products in polyethylene, polystyrene, and other solid organic polymers with low energy heavy ions. Seki et al.¹³ examined the cross-linking and the scission reactions in polysilane as a function of particle LET. There are still too few studies to know the detailed mechanisms in polymers due to the incident particle track structure. However, radiation chemistry experiments with heavy ions offer unique probes into the relative contribution of second-order processes in the formation of observed products.

An important application associated with the production of hydrogen is the radiolysis of the polymer materials mixed with nuclear waste. Hydrogen produced in the self-radiolysis of these polymer matrices causes difficulties in handling, shipping, and storage of the nuclear waste.^{17,18} α particles emitted by transuranic radionuclides and protons and carbon ions produced by neutron recoil reactions may lead to product yields completely different than that found with γ -rays. Since it is not yet possible to predict gas yields on the nature of polymers or the type of ionizing radiation, management of nuclear waste materials will rely heavily on experimental observations.

In the present paper, the molecular hydrogen yields of three polymers, polypropylene (PP), poly(methyl methacrylate) (PMMA), and polystyrene (PS), irradiated with protons and carbon ions of different energies have been investigated. The data have been combined with that from the radiolysis with γ -rays and helium ions on these polymers,¹⁹ and the studies with high-density polyethylene (PE),¹⁵ to give a comprehensive overview on the dependence of hydrogen yields on particle energy and linear energy transfer. These polymers have widely different functional groups on the side chain and make up a large portion of polymeric constructional materials.

Experimental Section

The polymer samples studied in the present paper were isotactic polypropylene (PP, 0.9 g/cm³, Aldrich and GoodFel-

low), poly(methyl methacrylate) (PMMA, 1.19 g/cm³, Good-Fellow), and polystyrene (PS, 1.05 g/cm³, Aldrich). The samples of PMMA and PS were free of added stabilizers, while the PP from GoodFellow contained small amounts of stabilizers to aid in the formation of sheets. Experiments with γ -rays on PP samples from different vendors showed that there was no variation in the yield of molecular hydrogen between the samples with or without stabilizers; it is assumed that the stabilizers in the PP are at too low of concentration to significantly affect the yield of molecular hydrogen. All the polymer samples were cut into pellets with a diameter of about 1 mm to minimize the influence of gas diffusion from the bulk polymer on the observed yields.¹⁵ The pellet surfaces were cleaned with distilled water and dried in a vacuum oven before irradiations.

Particle irradiations were conducted using protons and carbon ions from the 10 MeV FN Tandem Van de Graaff located in the Nuclear Structure Laboratory of the University of Notre Dame. The window assembly and irradiation procedure were essentially the same as previously reported.^{20,21} Particle energy was determined by magnetic analysis, and energy loss to the windows was calculated using standard stopping power tables.²² Absolute dosimetry was obtained by collecting and integrating the charge from the sample cell in combination with the particle energy. Beam currents were kept around 2 nA, and total energy deposited was usually $(1-5) \times 10^{18}$ eV within a few seconds. The ion beam diameter was 6.35 mm, and completely stripped ions were used so the particle flux was about $10^{11}/Q$ particles/(cm² s), where Q is the charge per particle. Such a low flux ensures that the tracks of incident particles are independent of each other and the overlap between tracks can be ignored.¹¹ The beam currents were also small enough to ignore the "target heating" effect due to the particle bombardments on polymers.^{23,24} The variation in sample configurations and range of particles gave a variety of absolute doses. Particle energy measurements and dosimetry are estimated to be better than 1%.

The sample cell for particle irradiation was made of quartz with a mica window about 5 mg/cm² thick. Ultrahigh purity argon was used as the carrier gas through the sample cell and to the detector with a flow rate of 50 mL/min. Hydrogen detection involved an inline technique similar to that previously described.^{15,19} A quadrupole mass spectrometer (Blazers, QMA140 analyzer with axially mounted SEM) was used to analyze the carrier gas downstream from the sample cell through a capillary tube ($\phi = 25 \mu\text{m}$, $L = 20$ cm). Hydrogen was observed at the mass-to-charge ratio of 2. Calibration of the system was conducted by injecting pure hydrogen gas with a micro-liter syringe. The relationship between H₂ volume and peak area was linear for all of the doses used. Total error in hydrogen measurement is estimated as $\pm 5\%$.

Results and Discussion

Hydrogen Yield in γ Radiolysis. γ radiolysis experiments were not performed in this work, but the radiation chemical yields are presented here because they are useful for comparing the radiolytic response between the different types of polymers and for examining the dependence of yields on the type of ionizing particle. Radiation chemical yields, G values, are presented in the traditional manner as molecules of hydrogen formed per 100 eV of total energy absorbed in the sample. The G values for molecular hydrogen are 3.3, 2.6, 0.24, and 0.033 molecules/100 eV of energy absorbed for PE, PP, PMMA, and PS, respectively, Table 1.^{15,19} The above G values are in good agreement with values measured in other laboratories, which verifies that the irradiation techniques and sample preparation

TABLE 1: Track Average Radiation Chemical Yields, G_0^a

particle	PE	PP	PMMA	PS
γ	3.30	2.58	0.240	0.033
H				
5 MeV	3.32	2.20	0.244	0.041
10 MeV	3.17	2.28	0.213	0.037
15 MeV	3.25	2.35	0.215	0.033
He				
5 MeV	4.63	3.15	0.621	0.151
10 MeV	3.78	2.51	0.411	0.095
15 MeV	3.52	2.38	0.307	0.074
20 MeV	3.37	2.25	0.254	0.064
C				
10 MeV	6.38	4.93	2.62	1.04
20 MeV	5.41	4.58	1.94	0.708
30 MeV	5.35	3.94	1.68	0.512

^a γ ray results from ref 19 and PE results from ref 15.

are suitable. The γ -rays have the smallest initial energy and the smallest energy deposition density of all radiation particles used in the present study. The initial energy of the γ -rays is about 1.25 MeV, and the corresponding linear energy transfer, LET, is around 0.2 eV/nm.

The yield of molecular hydrogen with γ -rays is obviously dependent on the polymer type. However, there is no reliable method for predicting the yields. The total carbon-hydrogen bond densities are 0.023, 0.014, 0.0069, and 0.0048 mol/cm³ for PE, PP, PMMA, and PS, respectively. The G values for hydrogen production have the same trend as the C-H bond densities, but the relative values do not agree. One may argue that only those C-H bonds on the main chain are damaged by the absorption of radiation and the various side groups respond as single entities. The main chain of polypropylene has 75% of the C-H bonds that polyethylene has, and its yield of hydrogen is about 75% of that with polyethylene. However, PS also has the same percentage of main chain C-H bonds, while PMMA has only 50%, and they have much lower molecular hydrogen yields. Reactions of the radicals after the C-H bond rupture are also important for the observed formation of hydrogen. The chemical nature of the side chain groups can have a large influence on the chemistry. Carbonyl and phenyl groups on the PMMA and PS, respectively, are good radical scavengers. It is possible that hydrogen atoms are formed with substantial yields in PMMA and PS, but addition, or self-scavenging, reactions lower the observed yield of molecular hydrogen formation.

Model compounds are sometimes used to predict hydrogen yields in polymers.^{25,26} Typically, these systems involve variation in carbon number, branching, and the temperature of liquid organics in order to estimate the radiation effects on condensed phase high molecular weight compounds. The results give reasonable predictions for hydrogen yields in polyethylene, but not polystyrene. A better estimate for hydrogen production in polystyrene can be obtained from liquid benzene.²⁷ The yield of hydrogen in liquid benzene is 0.038, which agrees well with the value of 0.033 in polystyrene. Further work is in progress, but it appears that in some cases the chemistry of the polymer can be similar to that of the side chain group alone.²⁷

Energy Dependence of Hydrogen Yields. The observed G values for protons, helium ions, and carbon ions for the four polymers are given in Table 1. Particle energies for these experiments vary from 5 to 30 MeV and cover the range near the end of the track where the linear energy transfer, LET (equal to the stopping power, $-dE/dx$) is changing significantly. The ranges of the particles are therefore relatively small and vary from 2.4 mm for 15 MeV protons to 0.013 mm for 10 MeV carbon ions in polystyrene.²² Small differences in ranges are

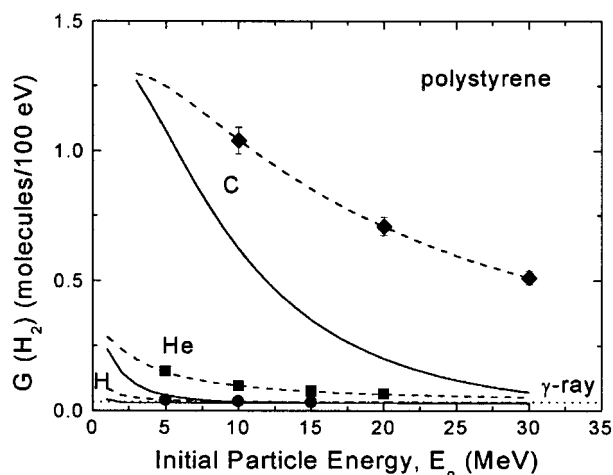


Figure 1. Dependence of molecular hydrogen yields in polystyrene on particle energy: (●) protons, (■) helium ions, and (◆) carbon ions. The dashed lines show the track average yields using eq 3 and the solid lines the track segment yields using eq 4. The dotted line shows the limiting γ -ray yield.¹⁹

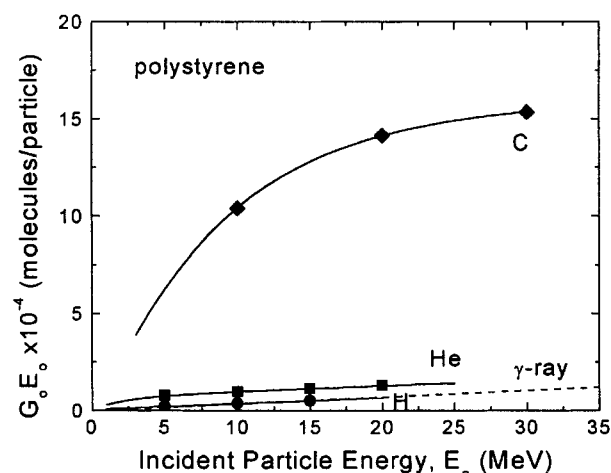


Figure 2. Total production of molecular hydrogen per incident particle, G_0E_0 , as a function of the initial particle energy, E_0 , with different particles in polystyrene: (●) protons, (■) helium ions, and (◆) carbon ions. The solid lines show the fit to the data using eq 2 and the dotted line shows the limiting γ -ray yield.¹⁹

found in the other polymers due to their slightly different structure and density. The sample thickness is much greater than the range of the particles in all cases so one is measuring a track average yield of all processes occurring from the incident particle energy to zero. A plot of the observed track average hydrogen yield, G_0 , for polystyrene as a function of particle initial energy is given in Figure 1. Somewhat similar graphs are found for the other polymers and can be easily constructed from the data in Table 1. The hydrogen yield is found to be very dependent on the particle type. For 10 MeV particles in polystyrene, the relative hydrogen yields are 1.0:2.6:28.1 for protons, helium ions, and carbon ions, respectively. Smaller, but observable, variations are found for the other polymers.

It is common to present radiation chemical yields as a function of particle energy like in Figure 1; however, it is more useful with heavy ion radiolysis to examine the data in the form in which it is collected. Figure 2 shows the production of hydrogen per incident particle, G_0E_0 , as a function of incident particle energy, E_0 . It can be seen that at energies above a few megaelectronvolts the rate of increase in the production of hydrogen is virtually the same for γ -rays, protons, and helium ions. Carbon ions show a sharp increase in hydrogen production

TABLE 2: Parameters Used in Analytical Equations

particle	PE	PP	PMMA	PS
H				
E_B	0.1	0.1	0.1	0.1
G_B	4.5	2.8	0.5	0.15
G_∞	3.2	2.2	0.21	0.03
a	6.348	2.571	0.548	1.740
m	0.963	0.606	1.998	1.194
He				
E_B	0.5	0.5	0.5	0.5
G_B	5.8	4.0	1.2	0.3
G_∞	3.2	2.2	0.21	0.03
a	0.0442	0.024	0.0884	0.290
m	2.057	2.512	1.923	1.152
C				
E_B	2.5	2.5	2.5	2.5
G_B	6.0	5.2	4.0	1.3
G_∞	3.2	2.54	0.24	0.03
a	0.0756	0.00063	0.332	0.0253
m	0.772	2.242	0.553	1.332

at low energies and at energy above 20–30 MeV hydrogen production appears to be approaching the same rate as that found with γ -rays. Common yields with high-energy particles are expected since LET decreases with increasing particle energy and the track structures of all heavy charged particles approach that of γ -rays.⁶

Comparison and manipulation of the data is made easier by describing the observed energy dependence of the yields by an analytical function. The function chosen is one that was successful in describing other similar data with heavy ions.²⁸ The sigmoidal character of the data in Figure 1 suggests an energy dependence of the form

$$G_0(H_2) = G_L + (G_\infty - G_L) [aE_0^m / (1 + aE_0^m)] \quad (1)$$

where G_L and G_∞ are the limiting yields at low and high energies, respectively, and the empirical parameters a and m are used to fit the specific set of data. These limiting yields and parameters are expected to reflect the rather complex processes that involve both second and higher order reactions and diffusion within the particle track as it relaxes.^{6,28}

The correct method of weighting the data requires fitting a plot of G_0E_0 as a function of E_0 . In addition, at low energies the radiation chemical yield approaches a maximum value of G_B at energy E_B corresponding to the Bragg peak where the energy loss is at a maximum. Very little is known about radiation chemical yields below the Bragg peak so it is assumed that the yield is constant at lower energies. Equation 1 can be modified to give G_0E_0 in the form

$$G_0(H_2)E_0 = G_BE_0 + (G_\infty - G_B)(E_0 - E_B)F \quad (2)$$

where F is a dimensionless factor given by

$$F = a(E_0 - E_B)^m / (1 + a(E_0 - E_B)^m) \quad (2a)$$

The values of G_∞ would normally be given by the γ -ray values. However, competing reactions in the proton and helium ion radiolysis in the energy range examined here may be giving slightly lower yields as discussed later. A nonlinear least-squares technique²⁹ was used to find the best fit of the data to eq 2, and the values of the parameters are given in Table 2. The solid lines in Figure 2 are obtained using the parameters in Table 2 with eq 2. The empirical fits describe the observed dependences very well for all the polymers and incident ions examined here.

Equation 2 is quite useful for describing a number of radiation chemical yields. For example, the track averaged radiation

chemical yield is obtained directly from eq 2 as

$$G_o(H_2) = G_B + (G_\infty - G_B)(1 - E_B/E_o)^F \quad (3)$$

The energy dependences predicted by eq 3 for polystyrene using the parameters in Table 1 are given by the dashed lines in Figure 1. The agreement with the experimental data for all of the polymers is good, which shows the self-consistency of the calculations.

These experiments measure track average molecular hydrogen yields because the particles are completely stopped in the sample. Differential, or track segment, yields give the radiation chemical yield in a thin sample where particle characteristics remain constant. There are many practical applications for such data such as in thin film irradiation. These yields are directly applicable to model calculations and aid in comparing the results of different particles. Track segment yields, G_i are equal to $d(G_o E_o)/dE_o$ and can be obtained from the fit of the data of Figure 2. Equation 2 can be modified to the following form to directly give the track segment yield consistent with the track average yield of eq 3.

$$G_i(H_2) = G_B + (G_\infty - G_B)[(1 + m)a(E_o - E_B)^m + (a(E_o - E_B)^m)^2]/(1 + a(E_o - E_B)^m)^2 \quad (4)$$

Track segment yields for polystyrene are shown as the solid lines in Figure 1. It can be seen that track segment and track average yields are similar at very low particle energies and they approach each other again at very high energies. By 30 MeV the track segment yields are similar for all of the ions examined here. Such a result is not too surprising for protons and helium ions. However, carbon ions at 30 MeV have a large LET and a track structure much different than that of γ -rays.⁶ Most of the additional hydrogen included in the track average yield for carbon ions in polystyrene is occurring at the end of the particle track. Similar conclusions can be made for the other polymers, except that the results are not as dramatic as in polystyrene. Obviously, the choice of the correct G value in practical applications and in comparison between different literature values is very important.

LET Dependence of Hydrogen Yields. The energy deposition density plays an important role in the radiolysis of polymers so it is desirable to relate the yields of molecular hydrogen explicitly to the linear energy transfer, LET, of the radiation. Track segment yields should be combined with differential LET values for model studies and in thin film irradiation. However, most practical applications involve relatively thick samples so in this work the track average yields will be examined as a function of track average LET.³⁰ Figure 3 shows the variation of track average molecular hydrogen yields with the track average LET for all the polymers and ion particles studied in the present paper. For γ -rays, the track average LET is about 0.2 eV/nm and the corresponding G values are shown as the limiting yields by dashed lines. It can be seen that all the polymers examined here show an increase in hydrogen yield with an increase in LET from ~ 0.2 eV/nm with γ -rays to ~ 800 eV/nm with 10 MeV carbon ions. However, the relative increase of molecular hydrogen yield with increasing LET is different for each polymer type. For example, with PE the G value increases about 93% from 0.2 eV/nm to 800 eV/nm. The corresponding increases for PP, PMMA, and PS, are 91%, 992%, and 3052%, respectively. Except for possibly a small decrease in hydrogen yield for PP and PMMA from γ -rays to protons and helium ions, the general trend of the data is an increase in hydrogen yields with increasing particle LET.

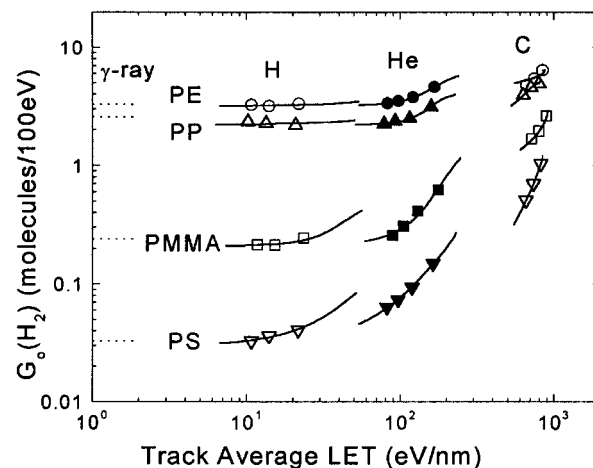
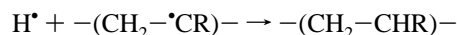


Figure 3. Dependence of molecular hydrogen yields on track average LET for the different polymers and particles: (●) high-density polyethylene, PE; (▲) isotactic polypropylene, PP; (■) poly(methyl methacrylate), PMMA; and (▼) polystyrene, PS. The dotted lines show the limiting hydrogen yields observed in γ -radiolysis. γ ray results from ref 19 and PE results from ref 15.

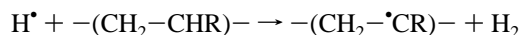
It is apparent from the data of Figure 3 that molecular hydrogen yields can be very dependent on the type of irradiating particle. The possible mechanisms involved will be discussed in the next section. However, many practical applications require only knowledge of product yields. It is clearly observed that the molecular hydrogen yields for one polymer with different types of radiation cannot be scaled from the corresponding data for another polymer. In other words, the "efficiency" for hydrogen production as a function of LET is different for each type of polymer. Even for a given polymer, it is incorrect to scale yields from one particle to another based solely on LET. Hydrogen yields with low-energy protons are greater than that of high-energy helium ions at the same LET. The particle track structure determines the local energy deposition density and thereby the concentration of initial transient species. Of two particles at the same LET, the particle with the greater charge will have a larger velocity with a resultant larger track radius and smaller local energy deposition density. LET is often a convenient parameter used to estimate energy deposition density, but in some systems it is not sufficient to predict product yields.

Radiation-Induced Reactions at High LET. Very few studies have examined the chemical reactions responsible for the observed increase in hydrogen yields with increasing particle LET. Knowledge from γ -ray or fast electron radiolysis would suggest that much of the molecular hydrogen production can be explained from simple radical chemistry following the C–H bond breakage. The following reactions involving the H atom are expected to occur.

recombination:



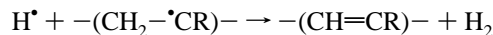
abstraction:



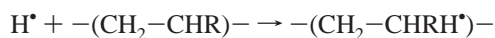
H–H combination:



disproportionation:



addition:



Recombination reactions are effectively an energy sink giving no observable products and lower the concentration of H atoms. Addition of the H atom to the carbon-carbon backbone is highly unlikely, and the chemical nature of the side group, R, will determine if addition occurs there. Aliphatic hydrocarbons largely undergo abstraction reactions and the yield of molecular hydrogen is usually large.³¹⁻³³ The relatively high molecular hydrogen yields for PE and PP suggest that H atom abstraction reactions are significant in these materials. Additional sources of molecular hydrogen are the unimolecular decomposition of the excited singlet state and the bimolecular reaction of the triplet excited state or the parent cation with molecules of the medium. These sources account for a large fraction of molecular hydrogen formation in the radiolysis of cyclic alkanes.³³ Their contribution to the formation of molecular hydrogen in the radiolysis of polymers is not known, but the effects of LET on H₂ yields may offer some suggestions, see below.

Increasing LET increases the local concentration of reactive species leading to an increase in radical-radical reactions. For those polymers in which abstraction reactions dominate, an increase in LET will lower the observed molecular hydrogen yield. This result will occur because hydrogen abstraction reactions lead to one molecule of hydrogen for every H atom while two H atoms are required for the H-H combination reaction. A slight decrease in molecular hydrogen yield from γ -rays to protons and helium ions may be present in PE and PP. Similar results were reported in the heavy ion radiolysis of cyclohexane.³¹

The disproportionation reaction for H atoms is very unfavorable in liquid hydrocarbons and is not expected to occur in polymers.³⁴ True disproportionation reactions involving carbon-centered radicals will also produce unsaturated products. Experiments by Dole indicate that only a small amount of vinylene groups are formed in the γ -radiolysis of polyethylene.³⁵ The low yield may be due to the difficulty for carbon-centered radicals to find each other in the widely separated energy loss events of γ -radiolysis. However, the increase in radical densities with increasing LET may raise vinylene yields significantly. Further experiments will be performed to examine vinylene formation.

Of the four polymers studied in this work, PMMA and PS have the lowest production of molecular hydrogen with γ -rays. The low yields may be due to the carbonyl and phenyl side chain groups, respectively. These groups are very effective radical scavengers and H atoms are expected to mainly add to them.^{36,37} Increasing LET will increase combination reactions with an observed increase in molecular hydrogen yields for these two polymers. However, such a large increase in molecular hydrogen yields as observed in the present studies indicates that H atom production in PMMA and PS is substantial. These polymers have been thoroughly studied, and the final products of the H atom addition reaction have not been identified in γ -radiolysis.¹⁻³ Polystyrene and liquid benzene appear to be radiation inert with γ -rays, and they have a remarkably similar hydrogen yield dependence on LET.²⁷ These data suggests that they both have the same mechanism for molecular hydrogen production. Benzene and polystyrene have high yields of excited states, but very little energy seems to be transformed to formation of final products.^{5,38} No products associated with the H atom adduct in liquid benzene have been observed with yields comparable to the observed molecular hydrogen formation at high LET.³⁹ Until products associated with H atom production

can be found in γ -radiolysis it can be assumed that H atom formation in polystyrene, and probably poly(methyl methacrylate), is negligible at low LET. Therefore, it appears that simple kinetics involving H atom reactions cannot explain the total observed increase in molecular hydrogen with increasing LET in polymers.

The data of Figure 3 suggests that the *G* values for molecular hydrogen production in the different polymers will converge at extremely large LET values. *W* values, or the energy to form an ion pair, are very similar for many organic liquids.⁴⁰ It can be expected that the yield of ionization does not vary significantly with the chemical structure of the solid polymer or the incident particle LET. Therefore, the formation and decay of the ionized species limit the maximum yield of polymer damage if no chain reaction is involved in the subsequent processes. Free radical formation may come directly from the degradation of ionic species or from excited states formed by neutralization reactions. The decay of ionic or excited species is normally very fast. However, high concentrations of these species can be found in the local regions of energy deposition by high LET particles. There are a number of phenomena that may occur in high LET tracks that are not found to any significance in γ -radiolysis. Neutralization reactions will not require diffusion of species since ion pairs will be in close proximity. Singlet to triplet state formation will be statistical, i.e., a ratio of 1 to 3, respectively, because of the homogeneous distribution of ionic species within the track.⁴¹ Energy will have little time to migrate through the molecular chain, if it can, before bond rupture occurs. The possibility for excited states to interact with each other or with other radiolytic products becomes significant. For instance, the fluorescence emission by excitons in the radiolysis of liquid benzene decreases with increasing LET.⁴² Any of these processes, or others, may be responsible for the high yields of molecular hydrogen formation at high LET. The existing data strongly suggest that increasing LET leads to an increase in the source of molecular hydrogen. The implications of these findings for high molecular hydrogen production are not only important in work with highly charged particles. High intensity lasers are equally capable of producing high concentrations of transient species. Hydrogen production could be significant in these situations provided there is sufficient energy to produce the appropriate state from the medium molecules.

Conclusions

The production of molecular hydrogen in the radiolysis of high-density polyethylene (PE), isotactic polypropylene (PP), poly(methyl methacrylate) (PMMA), and polystyrene (PS) by γ -rays, protons, helium ions, and carbon ions has been compiled and discussed. It was found that the production of molecular hydrogen per incident particle increases with particle energy and particle charge. Radiation chemical yields, *G* values, decrease with increasing particle energy. Track average hydrogen yields and track segment hydrogen yields are nearly the same at low particle energies. However, track segment yields rapidly decrease with increasing particle energy and they are nearly the same as that for γ -rays at energy above a few megaelectronvolts for proton and helium ions and 30 MeV for carbon ions. The results suggest that most of the excess hydrogen formation in track average yields is occurring near the end of the particle track.

The dependence of molecular hydrogen yields for the four polymers on particle linear transfer energy, LET, has been presented in a range from 0.2 eV/nm for γ -rays to 800 eV/nm for 10 MeV carbon ions. The yields of molecular hydrogen

generally increase with increasing particle LET. Polymers with low γ -radiolysis yields of molecular hydrogen such as polystyrene and poly(methyl methacrylate) have larger relative increases in yields with LET than the other polymers, polyethylene, and polypropylene. At very high LET the differences in hydrogen yield for the different types of polymers become smaller; i.e., the yields appear to be approaching a common value for all of the polymers. The data suggests that the observed increase in hydrogen yields with increasing LET is due to an increase in the source of molecular hydrogen and not due to a change in relative reaction rates. Further experimental information on both the yields of radiolytic products and of transient species in polymers irradiated with the particles of different LET values are necessary.

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