Production of Hydrogen in the Heavy-Ion Radiolysis of Polymers

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EMSP Need

Self-irradiation of waste materials is constantly changing their composition and thereby complicating environmental management decisions. One of the major problem products is gaseous molecular hydrogen, which can accumulate to explosive concentrations. Successful waste management of hydrogen producing materials requires an accurate determination of radiation chemical yields under a variety of conditions.

Information on the radiolysis of polymeric materials with γ-rays is available. However, heavy ions such as the α-particles produced by transuranic elements have a high rate of linear energy transfer (LET= -dE/dx) and can produce the same products with very different yields. The radiolytic mechanisms of polymers are not well understood so it is impossible to predict hydrogen, or other gas, yields.

Project Benefits

- The heavy ion research project at the University of Notre Dame is one of the few programs in the world that can routinely examine the radiation chemistry of materials with different types of charged particles.

- This project concentrates on the production of molecular hydrogen in the radiolysis of solid organic polymers and resins with heavy ions such as ^{1}H, ^{4}He, and ^{12}C.

- Radiation chemical yields obtained in this work can be applied directly to estimate risk due to molecular hydrogen formation in closed systems. The project also provides important fundamental knowledge on the decomposition mechanisms of polymers.

Summary of Results

- Molecular hydrogen yields in the radiolysis of high-density polyethylene, polypropylene, poly(methyl methacrylate), and polystyrene have been determined for H, He, and C ions.

- Hydrogen production with heavy ions can be very much greater than that observed with γ-rays. For instance, the H_2 yield in polyethylene with 5 MeV He ions is 40% greater than with γ-rays, but H_2 yield in polystyrene with 5 MeV He ions is 450% greater than with γ-rays.

- The mechanism responsible for H_2 formation is not known, but data collected by this project is helping to develop polymer model systems.

Particle Characteristics in Polyethylene

Particle	Energy (MeV)	Differential LET (eV/nm)	Average LET (eV/nm)	Range (mm)
^{1}H	2	17.0	37.2	0.070
	5	8.4	21.9	0.339
	10	4.8	14.0	1.17
	15	3.4	10.7	2.41
^{4}He	5	97.1	167	0.034
	10	58.8	121	0.102
	15	42.8	97.2	0.203
	20	33.8	82.4	0.336
^{12}C	10	748	843	0.012
	20	561	744	0.028
	30	450	663	0.048

$$\mathrm{LET} = -\,dE/dx$$

$$\overline{\mathrm{LET}} = \frac{1}{E_o}\int_o^{E_o} -\,dE/dx\; dE$$

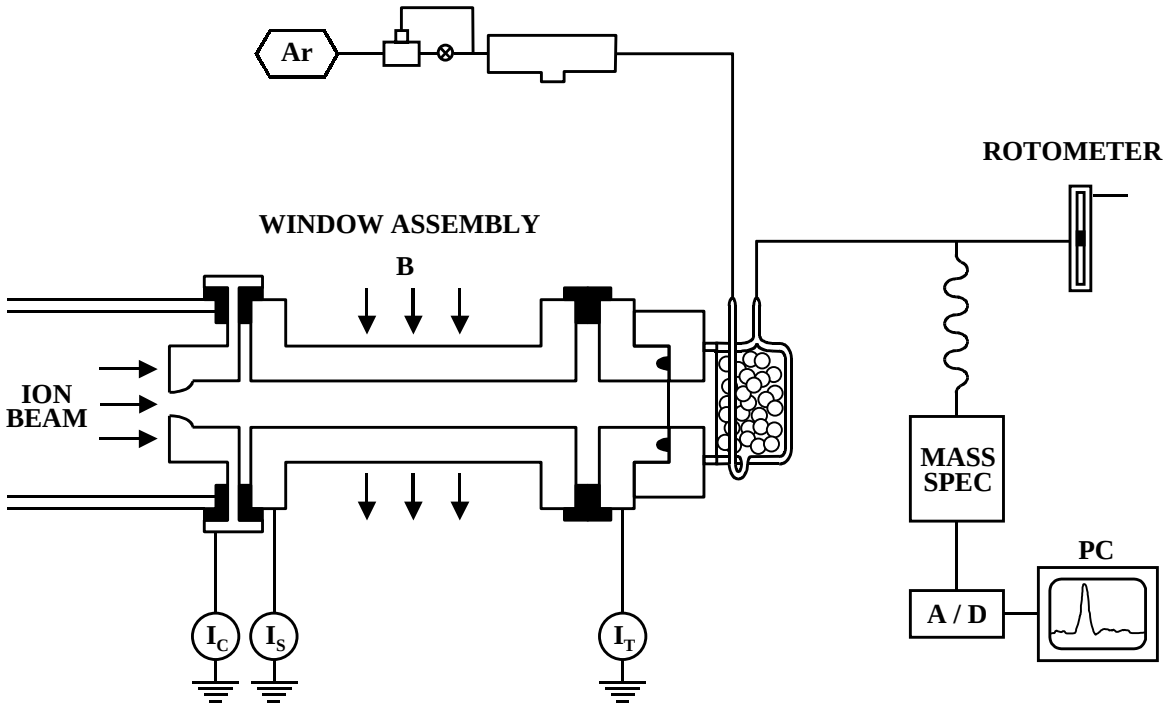
Experimental

Pellets of high-density polyethylene, polypropylene, polystyrene and poly(methyl methacrylate) were irradiated using the facility of the Notre Dame Nuclear Structure Laboratory. The particles pass through a window assembly that collimates the beam, suppresses scattered electrons, aligns the sample, and collects the total charge on the sample. Dosimetry is performed by integrating the collected charge in conjunction with knowledge of the particle charge and energy.

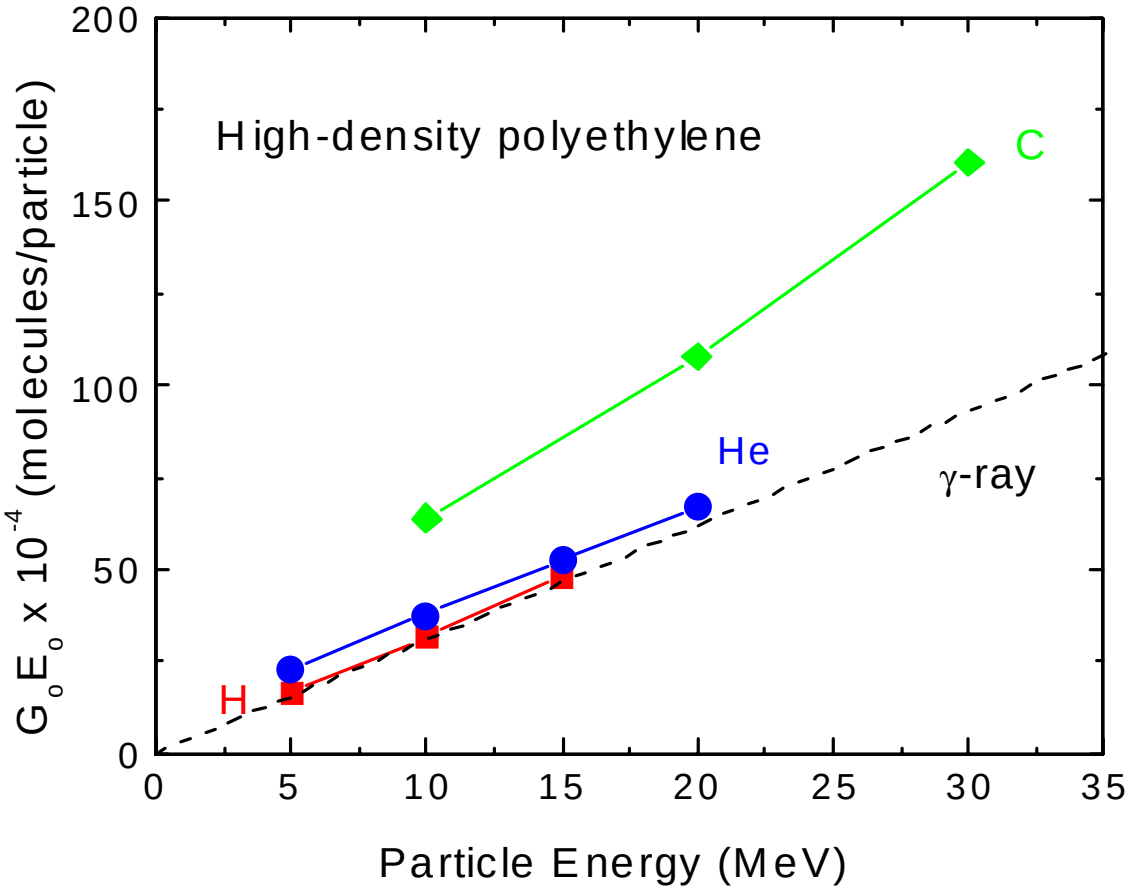
Hydrogen was collected by flowing a stream of Ar through the sample pellets and analyzing the effluent with a quadrupole mass spectrometer.

Gamma radiolysis was performed using a ^{60}Co source (~ 30 krad / min) with the same H_2 detection technique.

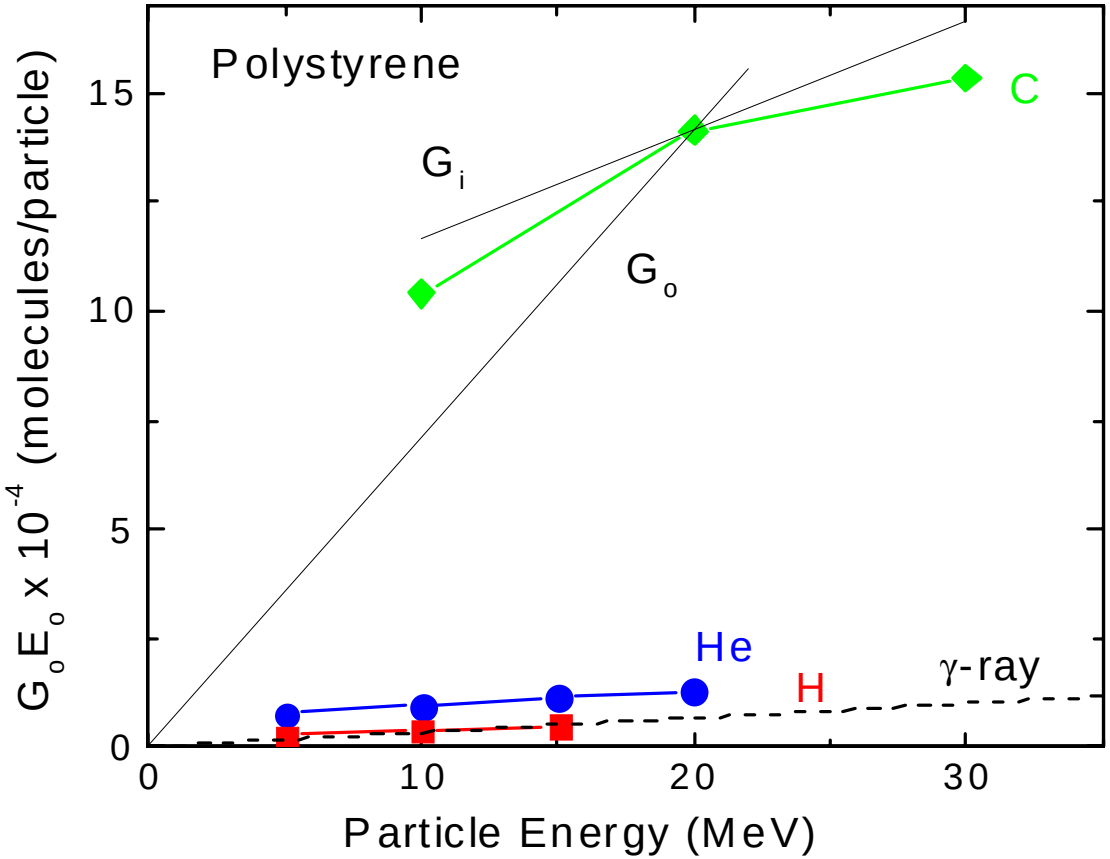
Heavy Ion Radiolysis Assembly



H_2 Production from Polyethylene



H_2 Production from Polystyrene

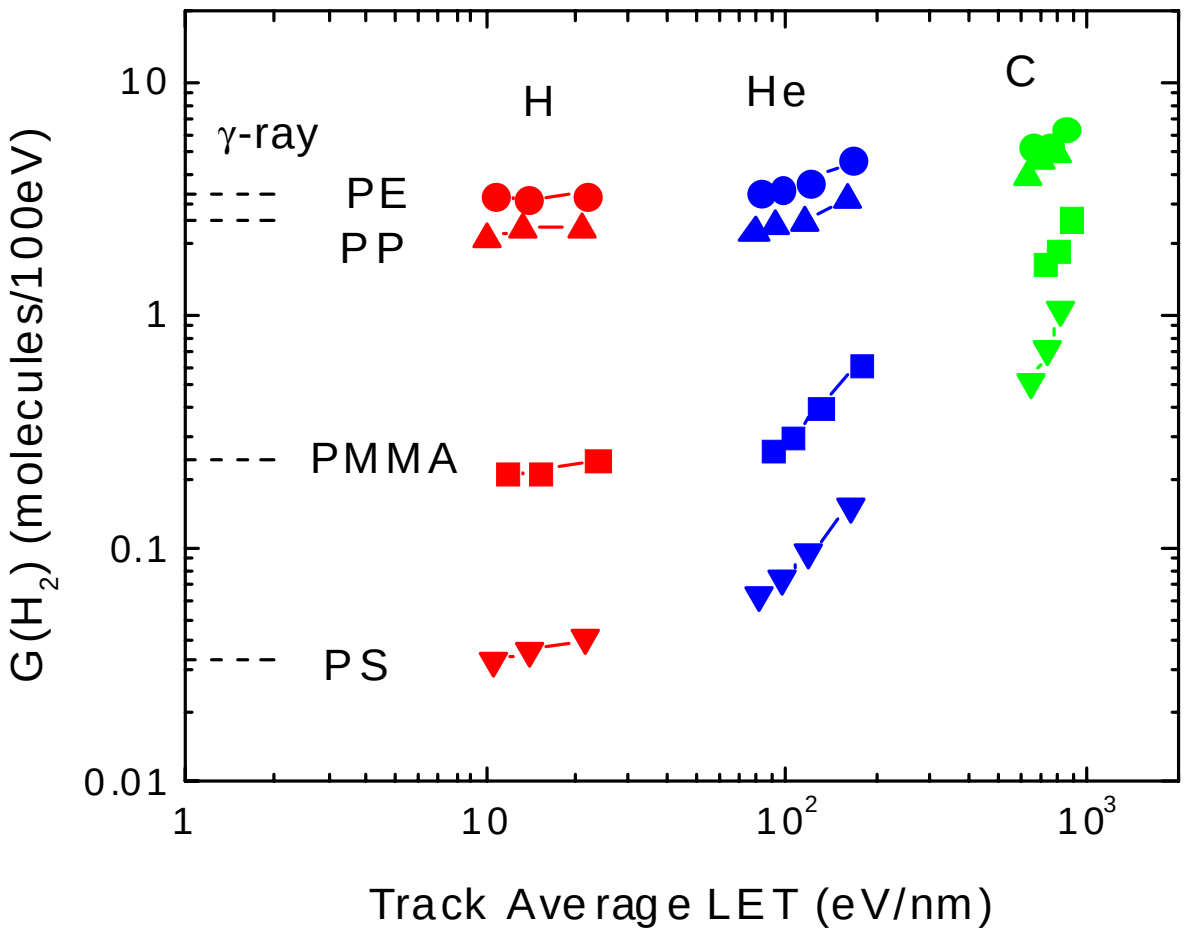


Track Segment H_2 Yields

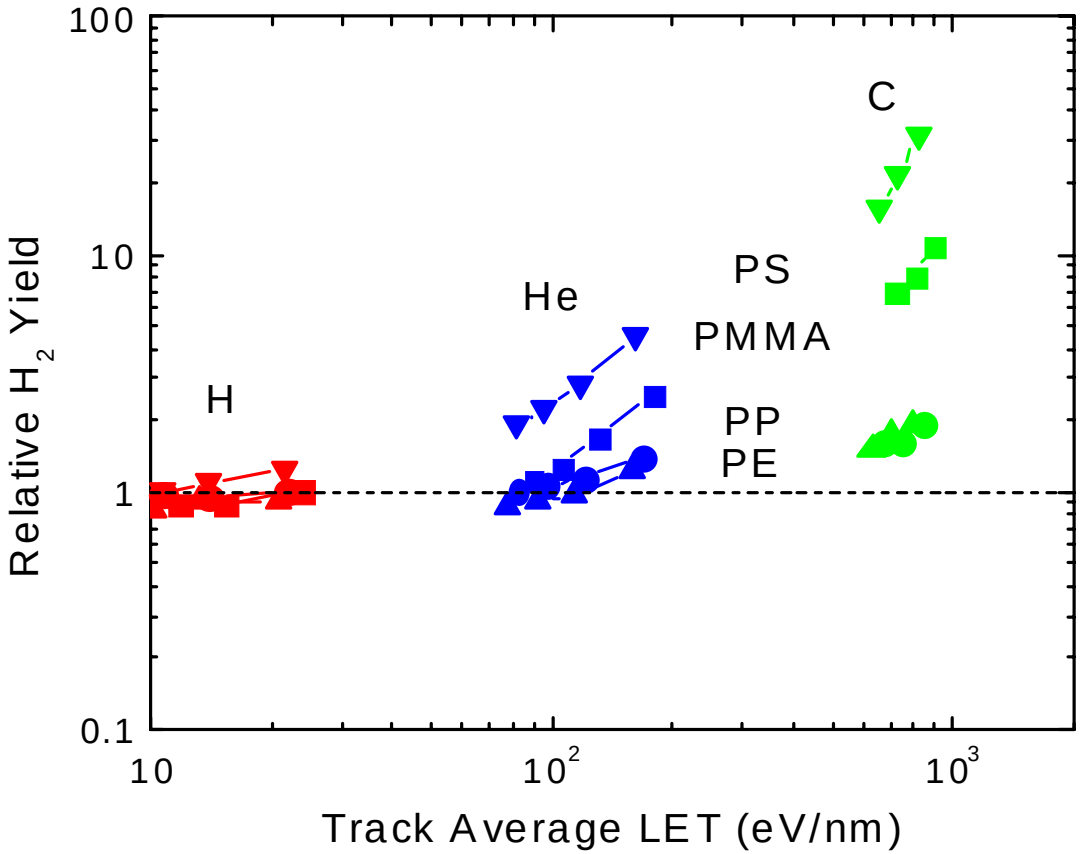
For all the polymers, the molecular hydrogen produced per particle (G_oE_o) increases with incident particle energy (E_o). The rate of increase is nearly constant for all the particles in the energy range examined, except possibly for carbon ions. The differential or track segment yield, G_i, at a given energy is equal to the slope of the tangent to the curve at that point. The data suggests that almost all the particles have similar track segment yields in the energy range examined here.

The curves in the G_oE_o plots all must pass through the origin. Therefore, at low energies the track segment yields approach the same value as the track average yields. The implication of these results is that most of the hydrogen is formed near the track end where the LET is the greatest.

Total Hydrogen Yield with Particle LET



Relative Hydrogen Yield with Particle LET



Track Average H_2 Yields

The dependence of the molecular hydrogen yields on particle LET has been determined for a wide LET range (from 0.2 nm/eV to 890 nm/eV). Track average yields are measured since the particles are completely stopped in the samples. It is found for all the polymers that the hydrogen yield increases with increasing particle LET. This increase can be substantial over the LET range examined here (3000% for polystyrene). The mechanism for the observed increase in H_2 yield with increasing LET is not known

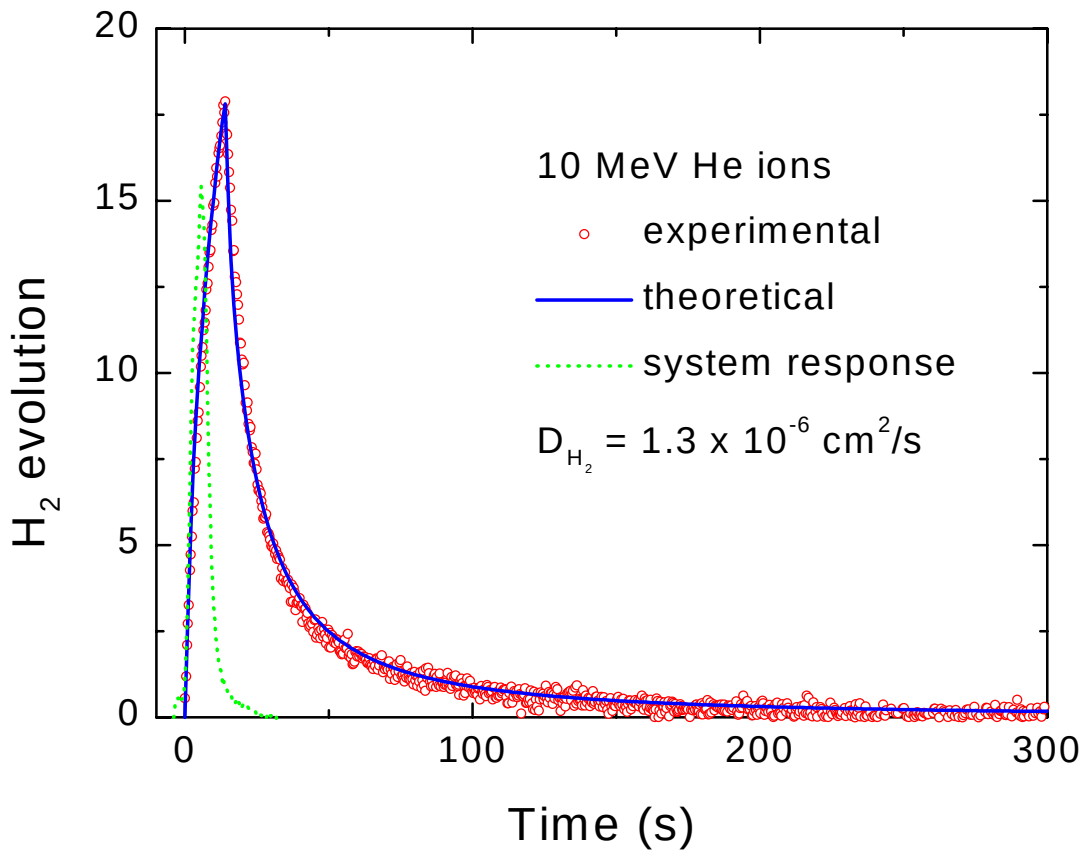
The data suggests that the limiting value for H_2 production at very high LET is about the same for all of the polymers examined here. It is assumed that total ionization is independent of LET, and $G(H_2)$ values may be approaching that limit. However, this assumption has not been proven.

Modeling of Hydrogen Diffusion

Examination of the H_2 evolution shows a much slower decay following the irradiation than the system response time. This slow decay is due to the limiting diffusion of the hydrogen to the surface of the bulk material. Experiments have shown that the H_2 decay with thick samples is independent of the gas flow, dose, and type of irradiating particle.

A simple one-dimensional model was used to predict the evolution of H_2 to the polymer surface by diffusion processes in the bulk material. The variable parameter in this model was the H_2 diffusion coefficient, which was determined to be about 1.5×10^{-6} cm^2/s and independent of the type of particle.

Time-scale of Hydrogen Diffusion



Radiation-induced Reactions Affected by Particle LET

As the ionization density increases with particle LET, the densities of excited states and free radicals increase resulting in a net increase in second order processes. H_2 formation can depend on a variety of reactions with different LET dependences.

Recombination	$H\bullet + -(CH_2-\bullet CR)- \rightarrow -(CH_2-HCR)-$
H-H *combination*	$H\bullet + H\bullet \rightarrow H_2$
Disproportionation	$H\bullet + -(CH_2-\bullet CR)- \rightarrow -(CH=CR)- + H_2$
Abstraction	$H\bullet + -(CH_2-HCR)- \rightarrow -(CH_2-\bullet CR)- + H_2$
C-C combination	$2-(CH_2-\bullet CR)- \rightarrow -(CH_2-`CR-`CR-CH_2)-$
Self-scavenging	$H\bullet + -(CH_2-HCR)- \rightarrow -(CH_2-HCRH\bullet)-$

Additional reactions between excited states or ionic species may also be responsible for the increase in hydrogen yield with increasing particle LET.

Future Efforts of Project

- The dependence of gaseous products other than H_2 on particle LET will be investigated in order to further elucidate reaction mechanisms and predict potential hazards from waste environments.

- Techniques such as spectroscopy and chromatography will be employed to get more information on other radiation products, such as cross-linking and chain scission.

- H_2 production in other polymers, such as polyvinyl alcohol, polybutylene, and poly(4-vinylpyridine) will also be examined for the dependence of yields on particle LET.