J. Phys. Chem. A **2008,** *112,* 3345−3351

Gas Production in the Radiolysis of Poly(vinyl chloride)

Jay A. LaVerne,*,†,‡ Eduardo A. Carrasco-Flores,† M. S. Araos,† and Simon M. Pimblott†,§,||

Radiation Laboratory, Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556, and School of Chemistry, Dalton Nuclear Institute, University of Manchester, Manchester, M13 9PL, U.K.

Received: December 3, 2007; In Final Form: January 28, 2008

The yields of H_2 and Cl^- were determined in the radiolysis of deaerated, aerated, and water mixtures of poly(vinyl chloride) (PVC) powders with γ-rays and 5 MeV He ions. H_2 yields with γ-rays are low at about 0.25 molecule/100 eV and they double with He ion radiolysis indicating a second order formation process. The production of H_2 in the γ-radiolysis of water-PVC mixtures is much greater than expected from the weight fraction of the components and is due to acidification of the aqueous phase by the evolution of HCl from the polymer. Cl^- yields in the γ-radiolysis of PVC with number average weights of 22 000, 47 000, and 99 000 Daltons are 19.6, 33.8, and 32.5 atoms/100 eV. Cl^- continuously evolves from the polymer for days following radiolysis. The extremely large yields suggest that a chain process involving radicals stabilized on the polymeric chain are responsible. Reflectance UV/vis and infrared spectroscopy show subtle changes in the PVC with radiolysis while UV/vis absorption spectra clearly indicate the formation of polyenes with 1 to 11 units. Cl^- formation is probably initiated by Cl radical production followed by an electron rearrangement mechanism along the PVC chain to produce more Cl^- and polyenes.

Introduction

Poly(vinyl chloride) (PVC) is a common polymer used extensively in construction and packaging materials exposed to ionizing radiation.[1] Applications include cable insulation, water pipes, medical devices, and pharmaceutical packaging that must withstand radiation environments or radiation sterilization that may alter its integrity or lead to the production of hazardous compounds. However, a mechanistic description of the behavior of PVC under irradiation has not been firmly established. The radiolytic degradation of PVC is important from a fundamental standpoint when it is compared to polyethylene or polystyrene. These compounds are essentially composed of a carbon−carbon backbone with or without aromatic side chains. The nature of side chains can have a huge effect on radiation stability. For instance, polyethylene shows moderate decomposition when irradiated, and polystyrene is generally considered to be radiation inert.[2] A detailed comparison of polymers with similar backbones may lead to the capability for predicting the radiolytic responses for a wide variety of similar compounds.

The earliest studies on the radiolysis of PVC identified the production of gaseous HCl and predicted radical precursors.[3−8] Along with HCl production, discoloration of the compound was readily apparent. Many of the early ideas on radiation damage in PVC came from observations of its thermal degradation, which established that the loss of chlorine atoms results in conjugation of the polymer chain by processes involving the production of radicals.[9−14] Variations in radiation effects following different thermal pretreatments were also shown.[15] Gas evolution studies found HCl to be the main component in radiolysis, but H_2 and other compounds were also observed.[16,17] Recent work has focused on the optical and magnetic resonance responses of irradiated PVC.[18,19] The early studies clearly established the main products, but quantitative analysis is still problematic. For instance, measured HCl yields vary by almost a factor of 2 depending on the radiation dose.[16] The wide variations of yields found in the literature further suggest that the mechanism is not understood and that certain critical parameters have not been identified.

Scissions of the C−Cl and C−H bonds of PVC are assumed to initiate the decomposition leading to gas production and to polyene formation, which is responsible for discoloration.[4,12] Polyene formation was originally proposed for PVC thermal degradation and subsequently assumed to occur in radiolysis. Environmental conditions can have a large impact on product yield. PVC irradiated under a vacuum has a yield of HCl of 2.3 molecules/100 eV, but that yield is 3.0 molecules/100 eV when irradiated in an O_2 environment.[16] The wide variety of product yields found in the literature suggests that a complete understanding of PVC radiolysis requires a more systematic approach where specific parameters are examined selectively. Furthermore, most of the literature addresses the radiolysis of PVC in a vacuum or in an O_2 atmosphere. Many practical applications involve PVC in intimate contact with water for which no study has been undertaken. An aqueous phase may stabilize reactive intermediates derived from PVC or water decomposition products may react with PVC leading to different products and/or yields.

In this work, the yield of the formation of Cl^- and H_2 from the radiolysis PVC with various amounts of water was determined. The PVC powder was further examined using a variety of spectroscopic techniques including reflectance and absorption UV/vis, diffuse reflectance infrared Fourier transform (DRIFT), and Raman. Gaseous products are correlated with the spectroscopic results. Irradiations were performed with γ-rays and with 5 MeV ^{4}He ions, the latter to simulate typical α-particle radiolysis occurring in PVC contaminated with actinides. Most commercial PVC contains stabilizers to mitigate some of the

---

* Corresponding author. E-mail: laverne.1@nd.edu.
† Radiation Laboratory, University of Notre Dame.
‡ Department of Physics, University of Notre Dame.
§ School of Chemistry, University of Manchester.
|| Dalton Nuclear Institute, University of Manchester.

10.1021/jp7113972 CCC: $40.75

thermal and radiation effects. Only pure PVC was examined in this work to establish the basic mechanisms and identify the appropriate intermediates to final, observed products. Once this baseline is established, other efforts will be better able to determine the effects of stabilizers.

Experimental Section

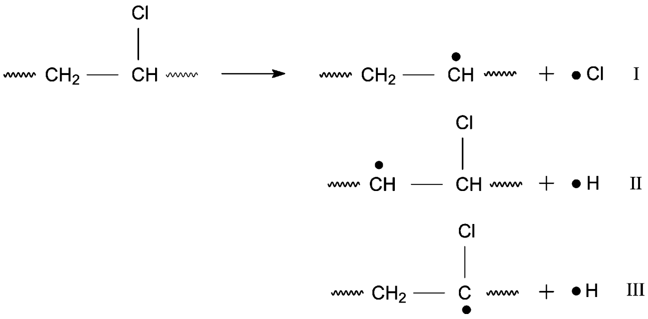
Materials. The PVC powders had number average molar masses, M_n, of 22 000, 47 000, and 99 000 with weight average molar masses of 43 000, 80 000, and 233 000, respectively. All the polymers were from Aldrich and contained no additives. They were outgassed by baking in a vacuum oven for 48 h at 50 °C. Typical water loading when exposed to 100% humidity is about 0.4 wt %. Particle area measurements were determined on a Quantachrome Autosorb 1 surface area analyzer by measuring nitrogen adsorption and desorption from the surface at an equilibrium vapor pressure using the Brunauer−Emmet−Teller (BET) method of surface area calculation. Specific areas of the three powders were similar at about 1.5 m^2/g, which correspond to particle diameters of about 3 mm assuming perfect spheres. Nano pure water (resistivity 18.7MΩ-cm) from an in-house H_2Only system (consisting of a UV lamp and several microporous ultrafilters) was used to prepare all mixtures.

γ-Radiolysis. Radiolysis with γ-rays was performed using a Shepherd 109 ^{60}Co source at the Radiation Laboratory of the University of Notre Dame. The dose rate was about 83 Gy/min as determined using the Fricke dosimeter.[20] The sample cell for the γ-irradiations was made from a 1 cm quartz cuvette with inlet and outlet ports for purging the sample before and after irradiation. Sample size was 0.5 g unless otherwise stated, and total doses were varied up to 100 kGy.

^{4}He Radiolysis. The ^{4}He ion irradiations were performed using the FN Tandem Van de Graaff facility of the University of Notre Dame Nuclear Structure Laboratory. The window assembly and irradiation procedure were the same as reported earlier.[21,22] Energy loss of the helium ions in passing through all windows was determined from a standard stopping power compilation.[23] The samples were irradiated with completely stripped ions at a charge beam current of about 1.5 nA. Absolute dosimetry was obtained from the product of the integrated beam current and the particle energy. The radiation chemical yields represent all processes from the initial particle energy to zero and are track averaged yields. The sample cell ($\phi \sim 1$ cm, $L \sim$ 0.3 cm) was made of quartz with a thin (∼4−6 mg/cm^2) mica window epoxied to the front for the beam entrance. Inlet and outlet ports allowed the cell to be purged before and after the irradiation. The use of absolute dosimetry directly gave the radiation chemical yield relative to the energy deposited in the entire sample. However, only a small portion of the total sample was actually irradiated ($\phi = 6.4$ mm, $L \sim 0.023$ mm) so the local dose rate is about 3.6 kGy/s. Irradiations were performed at room temperature (23 °C), and the dose rate was sufficiently small that no macroscopic heating was observed.

Gas Analysis. Hydrogen was determined in deaerated samples using an inline technique with a gas chromatograph. Ultrahigh purity argon was used as the carrier gas with a flow rate of about 50 mL/min. The argon passed through a constant flow regulator, an injection septum, and a four-way valve and into a 3 meter 5× molecular sieve column of an SRI 8610C gas chromatograph with a thermal conductivity detector. The sample was connected to the gas analysis system using the four-way valve, purged of air, isolated, irradiated, and then injected into the carrier gas stream. H_2 was determined in aerated samples and in water mixtures using flame sealed tubes ($\phi \sim 1$ cm, $L \sim$ 10 cm) that were irradiated and then crushed in the inlet line. Calibration of the detectors was performed by injecting pure H_2 with a gastight microliter syringe. Error in gas measurement was estimated to be about 5%.

SCHEME 1



Spectroscopic Analysis. The irradiated PVC powders were dried under ambient conditions and placed in sample cups for reflective spectroscopic analysis of the surface. DRIFT spectroscopy was performed using a Bruker Vertex 70 FT-IR spectrometer with a resolution 4 cm^{-1} and 512 scans in the range of 400−4000 cm^{-1}.[24] Raman spectroscopy was performed with a Renishaw Raman microscope using a 12 mW 514 nm laser source with a 1200 grooves/mm grating. Diffuse reflection UV/vis analysis was performed with an Ocean Optics USB2000 spectrometer, LS-1 tungsten-halogen lamp, and a R400−7 reflection/backscattering probe. Transmission UV/vis analysis was performed with an HP8453 diode array spectrometer.

Formation of Cl_2 was determined by the *N*, *N*-diethyl-p-phenylenediamine (DPD) colorimetric technique, EPA Method 330.5, using a Chemetrics I-2001 analytical kit.[25] This technique involves the hydrolysis of Cl_2 to the hypochlorite ion or hypochlorous acid followed by reaction with KI at pH 4 or less to give iodine. Iodine reacts with DPD to give a red color with two wide absorption bands at 510 and 550 nm. Calibration was performed with known NIST traceable Cl_2 standards.

Cl^- Determination. The Cl^- concentrations were measured using an ion chromatograph (Dionex model 500) having a 25 μL sample loop, IonPac AS11 (4 mm × 250 mm) analytical column, IonPac AG11 guard column (4 mm × 50 mm), Anion Self-Regenerating Suppressor (ASRS ULTRA), suppressed conductivity detector CD25, and a Dionex AS40 automated sampler. Remote operation of the instrument and data analysis was carried out using commercial software (Chromeleon, version 6.50). The eluent was a 6 mM NaOH solution at a flow rate of 1.5 mL/min. A suppresser current of 22 mA was applied to the auto suppressor. Under these conditions, the retention time was ∼1.8 min for Cl^- detection. Calibration was performed using standard solutions.

Radiation chemical yields, *G*-values, are given in units of molecules formed per 100 eV of total energy absorption to the PVC and any adsorbed water (1 molecule/100 eV $= 1.04 \times 10^{-7}$ mol/J).

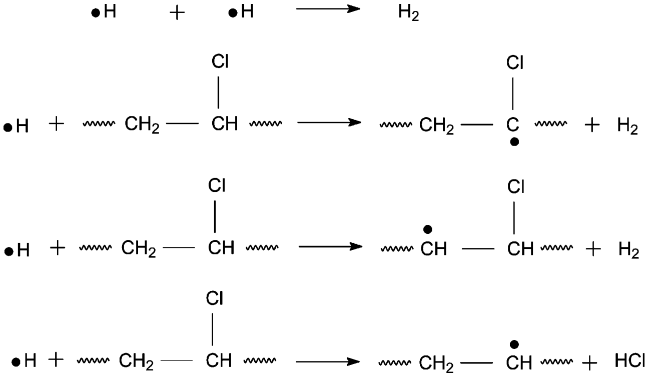
Results and Discussion

Initial Decomposition. The radiolytic decomposition of PVC was originally proposed by Chapiro.[4] Radical formation is initiated by cleavage of the C−H and C−Cl bonds, as shown in Scheme 1. The bond energies are 424 and 326 kJ/mol, respectively, so Cl atom production resulting in the formation of radical (I) is expected to dominate.[6,26] There is no direct determination of the strength of the two types of C−H bond (α and β to the Cl), but the radical formed by H atom loss by the

TABLE 1: H_2 Yields in the Radiolysis of PVC

condition	M$_n$	γ-rays	5 MeV He ions
deaerated	22 000	0.23	0.45
deaerated	47 000	0.27	0.41
deaerated	99 000	0.25	0.39
aerated	22 000	0.22	
wet/aerated	22 000	0.22−0.67	

SCHEME 2



methylene group, radical (II), is more unstable than radical (III).[6,19] Chain scission is also expected to a lesser extent with a subsequent loss of molecular weight.[4,6] Most of the observed radiation chemical products are expected to be due to the formation and subsequent reactions of the Cl and H atoms.

H_2 Production. Molecular hydrogen production is important in enclosed radiation environments where explosive concentrations may accumulate. The *G*-value for H_2 was found to vary from 0.23−0.27 molecule/100 eV in the γ-radiolysis of the three types of PVC in a deaerated atmosphere, Table 1. No systematic variation was observed with molecular weight and the small differences between the types of samples are probably due to systematic errors. The radiolysis of polyethylene and polystyrene under similar conditions gives yields of 3.3 and 0.04 molecule/100 eV, respectively.[2] The former yield is about half the expected maximum yield of 5−6 molecules/100 eV expected for typical aliphatic hydrocarbons, while all yields in most aromatics are very small.[27] Clearly, the stability of PVC with respect to H_2 production lies between these two extremes.

H_2 formation from H atom precursors can proceed by two main mechanisms, as shown in Scheme 2. Combination of two H atoms to give H_2 can occur, but this process requires the diffusion of H atoms and it is not expected to be dominant if other reactants for H atoms are available. Another pathway for reaction of the free H atom is to abstract an H atom from the parent PVC. Two different H atom donor groups are available and both will lead to the production of H_2.

Increasing the linear energy transfer (LET $= -\mathrm{d}E/\mathrm{d}x$) of the incident radiation leads to an increase in the local concentration of reactive species within the track. Second-order reactions become more favored over first-order processes. The heavy ion radiolysis of polyethylene and polystyrene show increasing H_2 yield with increasing LET.[2] PVC exhibits almost a doubling of the H_2 yields from the γ-radiolysis to the 5 MeV He ion radiolysis (see Table 1). These results indicate that H_2 is not formed mainly by a first-order process and therefore H atom abstraction reactions are negligible. The latter reactions of the H atom are expected to be common so the dominant reaction may be the abstraction of Cl atoms to give HCl instead of H atoms to give H_2. Similar processes have been observed in the radiolysis of aqueous solutions of the chlorinated methanes.[28] A relatively small amount of H_2 is formed by second-order combination processes that involve H atoms or excited states. H_2 yields show little dependence on the presence of oxygen so these second-order processes are too fast to be scavenged. Helium ion radiolysis shows a slight decrease in H_2 yield with increasing molecular weight of the PVC that is probably due to a local increase in density thereby slowing the second-order process responsible for H_2 production.

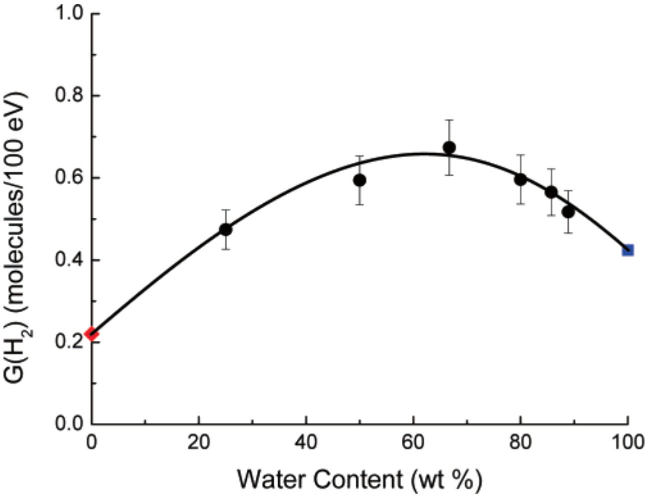


Figure 1. Production of H_2 in the γ-radiolysis of PVC (M$_n$ = 22 000) and deaerated water as a function of the water weight fraction. The dose of 10 kGy is determined with respect to the entire system.

H_2 production in the presence of liquid water has not been previous determined even though this environment is commonly encountered in many applications. Figure 1 shows the yields of H_2 in the γ-radiolysis of PVC (M$_n$ = 22 000) with various weight fractions of liquid water. Yields at the two extremes are simply those for deaerated PVC and neat water. However, the intermediate values are not linearly dependent on the water fraction. A maximum value of $G(H_2) = 0.67$ molecules/100 eV is observed at about 60 wt % water. The slight enhancement of H_2 is probably due to an increase in the hydronium concentration produced as the counterion to the Cl^- to be discussed below. The mixtures are becoming more acidic with radiolysis leading to an increase in H_2 production in the water phase. This increase is expected to be dependent on the total dose and can have significant consequences in many applications.

Cl_2 Production. Cl atoms produced by the initial PVC decomposition may combine to give Cl_2. Irradiations of PVC water mixtures were performed with γ-rays and with 5 MeV He ions of 100 and 500 kGy, respectively. Cl_2 rapidly hydrolyzes in water to give ClOH, which can readily be detected with standard water purity kits. No ClOH was detected in any of the irradiation mixtures suggesting *G*-values for the Cl_2 formation of less than 0.01 molecule/100 eV. Abstraction reactions of Cl atoms must dominate their chemistry with negligible competition from Cl−Cl combination reactions.

Cl^- Formation. In the studies of dry PVC, HCl is typically determined by measurement of the pressure or displaced volume of the head space gases following irradiation.[3−8,16,17] The extremely reactive nature of HCl may cause problems using this technique unless due care is taken. Also, other gases such as H_2 or CO_2 must be taken into account by condensation using a series of traps. This work measured the formation of Cl^- in a PVC−water mixture. Variations in amount of water had little effect as long as the PVC was covered by the liquid phase. HCl or Cl^- produced in the radiolysis was quickly solvated in

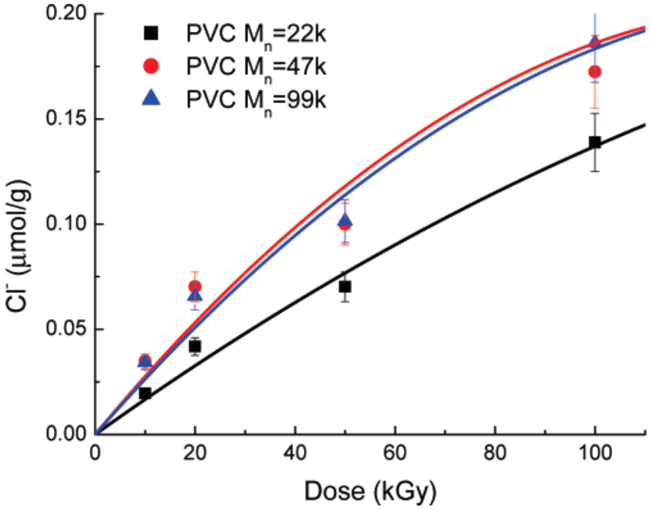


Figure 2. Production of Cl^- in the γ-radiolysis of PVC and aerated water mixtures as a function of dose: (■) M_n = 22 000; (●) M_n = 47 000; (▲) M_n = 99 000.

TABLE 2: Cl^- Yields in the Radiolysis of PVC

condition	M_n	γ-rays	5 MeV He ions
wet/aerated	22 000	19.6	1.18
wet/aerated	47 000	33.8	
wet/aerated	99 000	32.5	

the aqueous phase. Throughout this work, the yield of Cl^- is assumed to represent that of HCl.

In agreement with the literature, this work finds that the major product in the radiolysis of PVC is Cl^-.[3−8,16,17] Figure 2 shows the formation of Cl^- as a function of the dose for the three different types of PVC. Low-dose yields are found to be 19.6, 33.8, and 32.5 atoms/100 eV for number average PVC molecular weights of 22 000, 47 000 and 99 000, respectively, (Table 2). Unlike H_2 formation, there is a noticeable difference in Cl^- yields with PVC molecular weight, and its production is not linear with dose. Several indicators suggest that the formation of Cl^- is not completely due to a direct action of radiation on PVC.

The yields of Cl^- were observed to depend on the time interval between radiolysis and analysis. A considerable amount of post-radiolysis delay is required before Cl^- yields become stable, that is, invariant with further delay time. In practice, the yield of Cl^- was found to be constant after 2−3 days depending on the dose. The production of Cl^- given in Figure 2 was measured after a delay of 5 days to ensure completion of the radiation-induced processes. Yields measured immediately after radiolysis were only about 2−3 atoms/100 eV, which are similar to the results observed by other investigators and consistent with radiation chemical *G*-values for energy transfer events.[17] Literature values for HCl yields in pure PVC vary from about 1.8 to 27 molecules/100 eV.[3−8,16,17] Once the yields were allowed to stabilize, the measurements were very reproducible. Increasing the dose rate leads to a decrease in HCl yield.[5] Radiolysis with He ions leads to an effective high local dose rate compared to γ-radiolysis and a decrease in Cl^- yield from 19.6 to 1.2 atoms/100 eV (Table 2). These observations suggest that a slow chain process is responsible for most of the Cl^- production. High dose rates or high LET leads to decomposition or quenching of the precursor to Cl^-. Previous EPR studies found a very long decay time for radicals produced in PVC radiolysis.[3] About 50% of the initially produced radicals survived for at least 4 h and 20% remained for up to 80 h following the radiolysis of PVC at 55 °C. Far longer times may be expected for the lower temperatures of this study. Because this work focuses on the gas production and spectroscopic studies, no attempt was made to examine the correlation between the rates of radical decay and Cl^- formation.

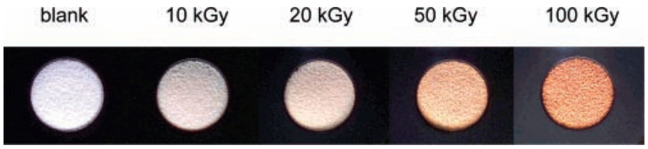


Figure 3. Discoloration of PVC (M_n = 22 000) in γ-radiolysis to different total doses.

The maximum yield of radiolytic species produced by the direct decomposition of organic compounds is found to be about 5−6 molecules/100 eV.[27] This limit arises from the nearly constant ionization yields for the parent compounds. Significantly higher yields are indicative of a chain process in which a radical precursor produces a stable product and an additional radical that repeats the process until termination by reactions of two radicals or quenching by an impurity. The high observed yields of 20−30 atoms of Cl^- per 100 eV suggest that a chain process is responsible for its formation. Post radiolysis effects indicate that the chain process is very slow and must be due to a radical or other energetic state that is stabilized on the polymer backbone.

Spectroscopic Studies. PVC has been reported to turn dark with radiolysis or thermal degradation due to the formation of unsaturated sites.[4,12] Figure 3 shows the progressive darkening of PVC upon γ-radiolysis of up to 100 kGy. A color change is observable immediately following radiolysis even at the very lowest doses. UV/vis reflection studies were performed on deaerated, aerated, and water mixtures of PVC (M_n = 22 000). Samples were irradiated with γ-rays to a given dose, and those covered with water were subsequently dried. The resulting UV/vis spectra are given in Figure 4 as a function of dose for the three different environments. Two broad bands at 500 and 800 nm are observed with little or no detailed structure. No significant variations are apparent in the spectra for the three environmental conditions. The literature contains a variety of explanations for the transitions responsible for the observed UV/vis spectra, but an extensive study has eliminated the possibility of a charge-transfer complex or a carbonium ion.[29]

Mixtures of PVC (M_n = 22 000) and water were irradiated with γ-rays, subsequently dried under ambient conditions, and then examined using DRIFT spectroscopy to identify specific bond features. DRIFT spectra are shown in Figure 5 as a function of radiation dose. Similar spectra were observed for deaerated and aerated PVC. No variation in the C−Cl bonds is observed at the low conversions used in this work due to the large total absorption in that spectral region. A small decrease in the CH_2 stretch mode with increasing dose may be associated with H atom formation by cleavage of the C−H bond. An increase in the formation of C═O and OH is probably due to oxygen addition to radicals on the PVC carbon backbone. Residual oxygen is common in PVC, and simple deaeration is not sufficient to eliminate gases completely from the bulk polymer. Heat and high vacuum are required to draw out absorbed oxygen. Therefore, products derived from oxygen reactions with radicals produced by PVC degradation are expected.

Reflectance spectroscopy examines the PVC powder surface, and the spectra are not very sensitive to the relatively small conversions associated with the doses given in this work. Irradiated PVC samples were dissolved in THF and reexamined using UV/vis absorption spectroscopy. The absorption spectra

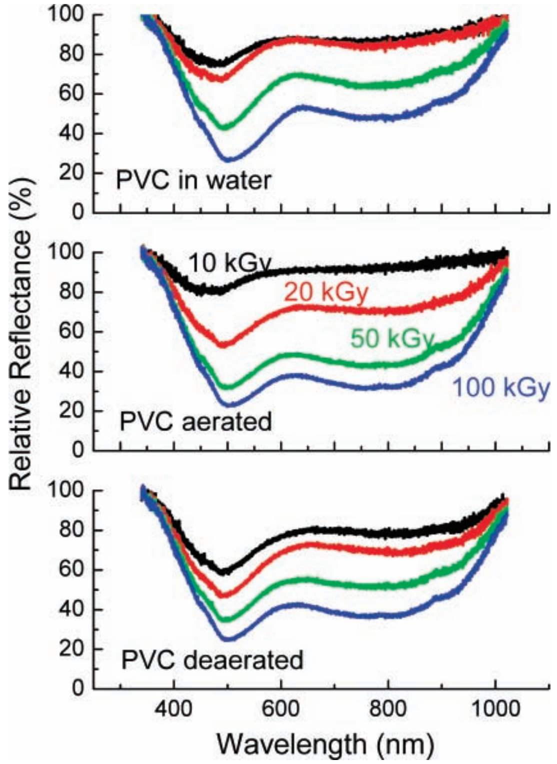


Figure 4. UV/vis reflection spectra of deaerated, aerated, or a water mixture of PVC (M_n = 22 000) as a function of dose following γ-irradiation.

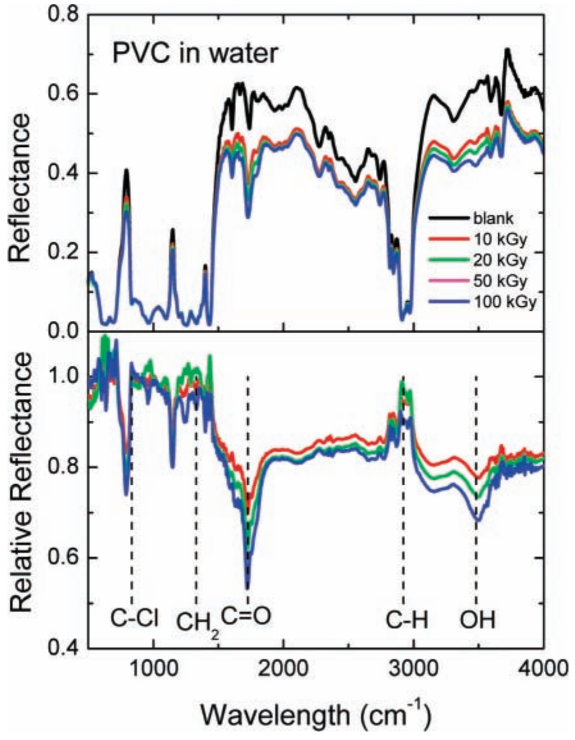


Figure 5. Diffuse reflectance infrared Fourier transform, DRIFT, spectra of PVC (M_n = 22 000) as a function of dose following γ-irradiation of a water mixture with subsequent drying.

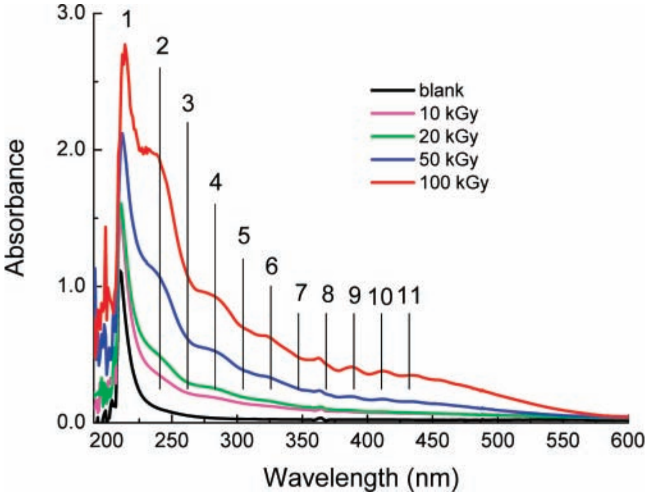


Figure 6. Transmission UV/vis spectra of PVC (M_n = 22 000) as a function of dose following γ-radiolysis and dissolving in THF. The vertical lines indicate the expected wavelengths for absorption maxima with the given number of double bonds.

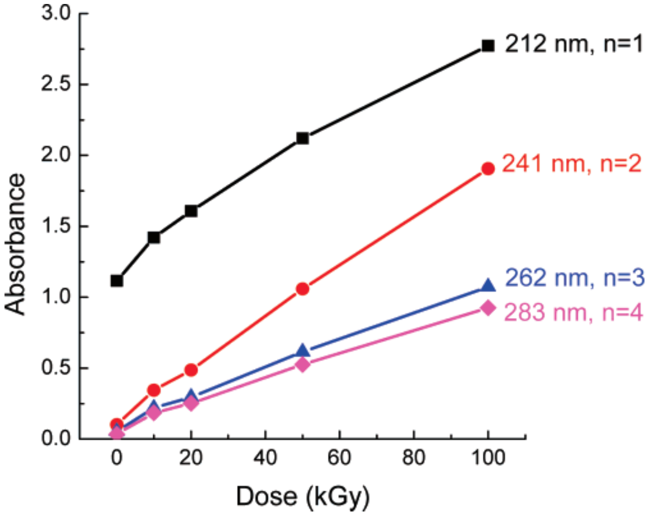
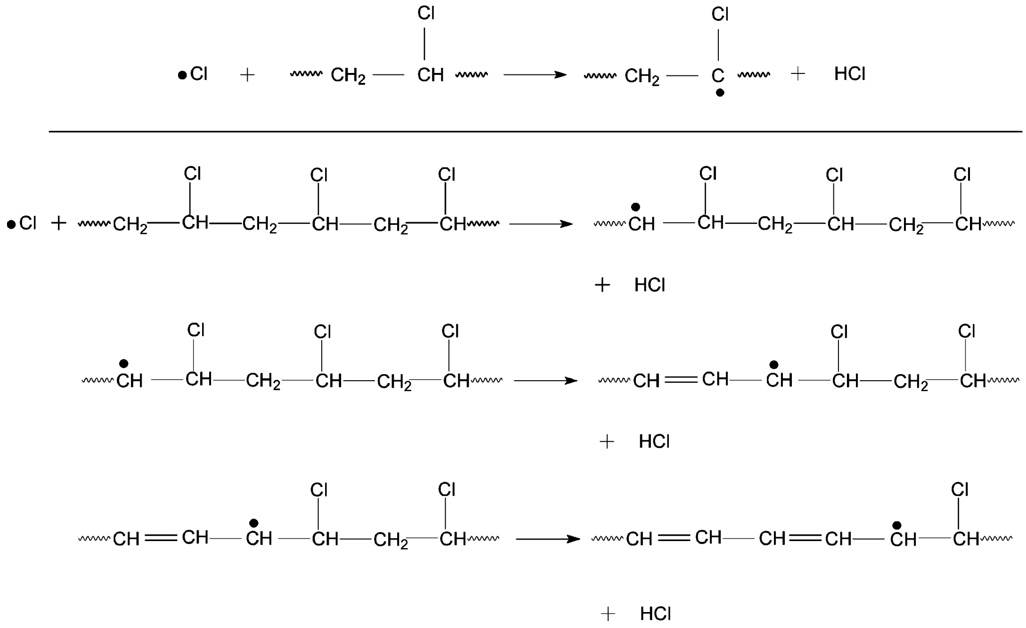


Figure 7. Variation in the absorbance of PVC (M_n = 22 000) at different wavelengths corresponding to the listed number of double bonds in Figure 6 as a function of dose in γ-radiolysis.

shown in Figure 6 have more of the fine structure commonly associated with thermal degradation of PVC.[3,7] Spectra obtained from room temperature γ-ray irradiations do not seem to have been published, and the results from low-temperature irradiations are somewhat similar to those observed in this work.[7] The large peak at 212 nm increases with increasing dose and a series of fine structure peaks tail off at higher wavelengths. The peak at 212 nm is due to vinyl chloride as determined by the absorbance of a solution of the pure compound. Vinyl chloride is the monomer used to make PVC, and residual contamination is to be expected. However, vinyl chloride or something similar is also formed by radiolysis. Figure 7 shows the linear increase in the absorbance at 212 nm with increasing dose. There is also a slight shift in the peak maximum to the red, which probably represents the small difference in absorption of monomeric vinyl chloride and a single unsaturation site along a PVC backbone.

Previous thermal degradation studies observed absorption spectra with similar fine structure to that found in this work.[3,13,14] The fine structure is attributed to the formation of a series of conjugated C═C double bonds along the PVC carbon backbone. A zipper mechanism was suggested to account for the formation of the series of conjugated bonds following the abstraction of an H atom from the polymer by a free Cl atom.[9,12] The resulting radical is unstable, and a series of elementary electron-transfer reactions lead to the further elimination of Cl^- while propagating the unsaturation down the polymer chain (Scheme 3). Each successive peak at the higher wavelength corresponds to a longer

SCHEME 3



chain of unsaturation. The thermal degradation work of Abbas and Sorvik lists the wavelengths associated with polyene sequence lengths of 3−12 units and shows that the wavelength gap between absorption maxima is constant.[13] The wavelength gap of that work was scaled to the main vinyl peak at 212 nm to give a prediction of the wavelengths expected for each unit increase of the polyene sequence in this work. The predictions labeled in Figure 6 for 2−11 unsaturated units match well with many of the observed absorbance maxima. Polyenes of up to 11 units can be readily observed with doses of 100 kGy. Discoloration of a polymer is usually associated with the formation of 7 polyene units, but the photograph of PVC in Figure 3 clearly shows darkening with doses as low as 10 kGy with little other than the formation of 1−2 polyenes.[12] The increase of the 1−4 conjugated double bond moieties with increasing dose is shown in Figure 7. Both the 1 and 2 unit moieties seem to be linear with dose, but the higher order polyenes are not. Similar observations for the higher order polyenes were made before.[14] Each of the polyenes is the result of the propagation of a radical down the PVC chain. This propagation results in the chainlike formation of Cl^- on a relatively long time scale. High dose rates or doses, high LET, or defect sites interfere with this process and limits the Cl^- yield.

Conclusions

The yields of H_2 and Cl^- were determined in the radiolysis of deaerated, aerated, and water mixtures of PVC powders with γ-rays and 5 MeV He ions. The production of H_2 in the γ-radiolysis of water-PVC mixtures is much greater than expected from the weight fraction of the components and is due to acidification of the aqueous phase by the evolution of HCl from the polymer. H_2 is produced by a second-order process that involves combination of H atoms or parent excited states. The extremely large yields of Cl^- and its slow rate of formation suggest a chain process involving radicals stabilized by the polymeric chain are responsible. Reflectance UV/vis and infrared spectroscopy show subtle changes in the PVC spectrum with radiolysis, and UV/vis absorption spectra clearly indicate the formation of polyenes with 1−11 units. Cl^- formation is probably initiated by Cl radical production followed by an elementary electron transfer along the PVC chain to produce more Cl^- and polyenes.

Acknowledgment. The authors thank Professor Michael Wiescher for making the facilities of the Notre Dame Nuclear Structure Laboratory available. The latter is funded by the National Science Foundation. This research was supported by the Office of Science (BER), U.S. Department of Energy, and Grant DE-FG02-04ER63744. This contribution is NDRL-4756 from the Notre Dame Radiation Laboratory, which is supported by the Office of Basic Energy Sciences of the U.S. Department of Energy.

References and Notes

(1) Nicholson, J. W. *The Chemistry of Polymers*, 2nd ed.; The Royal Society of Chemistry: Cambridge, U.K., 1997.
(2) Chang, Z.; LaVerne, J. A. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1656.
(3) Atchison, G. J. *J. Appl. Polym. Sci.* **1963**, *7*, 1471.
(4) Chapiro, A. *J. Chim. Phys.* **1956**, *53*, 895.
(5) Decker, C. *J. Appl. Polym. Sci.* **1976**, *20*, 3321.
(6) Miller, A. A. *J. Phys. Chem.* **1959**, *63*, 1755.
(7) Ohnishi, S.; Nakajima, Y.; Nitta, I. *J. Appl. Polym. Sci.* **1962**, *6*, 629.
(8) Arakawa, K.; Seguchi, T.; Yoshida, K. *Radiat. Phys. Chem.* **1986**, *27*, 157.
(9) Fuchs, W.; Louis, D. *Makromol. Chem.* **1957**, *22*, 1.
(10) Geddes, W. C. *Rubber Chem. Technol.* **1967**, *40*, 177.
(11) Thallmaier, M.; Braun, D. *Makromol. Chem.* **1967**, *108*, 241.
(12) Winkler, D. E. *J. Polym. Sci.* **1959**, *35*, 3.
(13) Abbas, K. B.; Sorvik, E. M. *J. Appl. Polym. Sci.* **1975**, *19*, 2991.
(14) Tudos, F.; Kelen, T.; Nagy, T. T.; Turcsanyi, B. *Pure Appl. Chem.* **1974**, *38*, 201.
(15) Zhao, W.; Yamamoto, Y.; Tagawa, S. *J. Polym. Sci. A: Polym. Chem.* **1998**, *36*, 3089.
(16) Hegazy, E. A.; Seguchi, T.; Machi, S. *J. Appl. Polym. Sci.* **1981**, 2947.
(17) Zahran, A. H.; Hegazy, E. A.; Eldin, F. M. E. *Radiat. Phys. Chem.* **1985**, *26*, 25.
(18) Baccaro, S.; Brunella, V.; Cecilia, A.; Costa, L. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2003**, *208*, 195.
(19) Costa, L.; Brunella, V.; Paganini, M. C.; Baccaro, S.; Cecilia, A. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2004**, *215*, 471.
(20) Pastina, B.; LaVerne, J. A.; Pimblott, S. M. *J. Phys. Chem. A* **1999**, *103*, 5841.
(21) LaVerne, J. A.; Schuler, R. H. *J. Phys. Chem.* **1987**, *91*, 6560.
(22) LaVerne, J. A.; Schuler, R. H. *J. Phys. Chem.* **1987**, *91*, 5770.

(23) Ziegler, J. F.; Biersack, J. P.; Littmark, U. *The Stopping and Range of Ions in Solids*; Pergamon: New York, 1985.
(24) Mitchell, M. B. *Adv. Chem. Ser.* **1993**, *236*, 351.
(25) *Chlorine, Total Residual. Methods for Chemical Analysis of Water and Wastes: 330.5*; Environmental Protection Agency, U. S. Department of Commerce: Washington, DC, 1983.
(26) Benson, S. W. *Thermochemical Kinetics*; John Wiley and Sons, Inc.: New York, 1968.
(27) Gyorgy, I.; Wojnarovits, L. Basic Processes in Hydrocarbon Radiolysis, and Methods for Investigating Them. In *Radiation Chemistry of Hydrocarbons*; Foldiak, G., Ed.; Akademiai Kiado: Budapest, 1981; pp 17.
(28) Pimblott, S. M.; Milosavljevic, B. H.; LaVerne, J. A. *J. Phys. Chem. A* **2005**, *109*, 10294.
(29) Gerrard, D. L.; Maddams, W. F. *Polym. Comm.* **1984**, *25*, 185.