Mechanistic Study on the Radiolysis of Dilute PVA Aqueous Solutions

Shu-Juan Zhang and Han-Qing Yu*
Department of Chemistry, University of Science & Technology of China, Hefei, Anhui, 230026, P. R. China

(Received January 14, 2004; CL-040054)

The mechanisms behind the radiolytic degradation of PVA in dilute aqueous solutions were elucidated. The formation of hydrogen as the main gaseous product, as well as the analysis of degradation intermediates by NMR, FTIR, UV–vis, and viscosity determination demonstrated that the mechanism of the radiolytic degradation of PVA was hydrogen abstraction, followed by chain scission.

Because of its water-solubility and excellent resistance to scents, flavors, oils, and fat, polyvinyl alcohol (PVA) is widely used as warp sizing and paper coating agents, adhesives and films. Although PVA is biodegradable under both aerobic and anaerobic conditions,[1] its degradation is very slow even with carefully selected microorganisms and under favorable conditions.[2,3] Consequently, the large amount of discharged PVA from industrial effluents has become a significant environmental problem.

Ionizing radiation has proven to be a promising alternative for the treatment of PVA-rich wastewaters.[4,5] Experiments performed under different gas saturation (O_2 or N_2) and with addition of various radical scavengers (*t*-BuOH, 2-PrOH and H_2O_2) have demonstrated that •OH played the key role in radiolytic degradation of PVA and that H• played a minor role.[5] Monitored by the reaction with tetranitromethane, the radiolysis of PVA has proven to be initiated by hydrogen abstracting.[6] The •OH radicals can either abstract a H-atom in α-position to the OH-group or from the neighboring methylene group (β-position), leading to the formation of radical intermediates which then underwent further chain scission, disproportionation or crosslinking.[6] Sakumoto and Miyata reported that in the presence of oxygen the attack of •OH radicals on methylene groups led to a scission of main chain, yielding low molecular weight products such as acids, aldehydes, and alcohols. In the absence of oxygen such attack caused the formation of crosslinked high molecular weight polymers with carbonyl groups.[4] However, no detailed information about the radiolytic degradation products of PVA is available. Owing to their resistance to organic solvents, experimental difficulties are encountered in the identification of PVA degradation intermediates. As a result, mechanistic information about the radiolytic degradation of PVA in aqueous solutions is still limited. Therefore, in this work, our efforts focused on the mechanistic characterization of PVA radiolytic degradation in aqueous solutions, in order to provide useful information for the utilization of ionizing radiation as a pretreatment method for refractory pollutants.

PVA [average degree of polymerization (DP): 1750 ± 50, degree of hydrolysis: 98%], boric acid, iodine, potassium iodide, deuterated dimethyl sulfoxide (DMSO-d_6), all purchased from Shanghai Chemical Reagent Company, were of analytical reagent grade and were used for experiments without further purification. Throughout the experiments, samples with an initial PVA concentration of $0.25\,\mathrm{g\,L^{-1}}$ were prepared with doubly distilled water in Pyrex glass vessels and irradiated by a ^{60}Co-γ-source.

The evolution of the UV–vis absorption of PVA aqueous solutions prior to and after irradiation was recorded both directly and after addition of boric acid and iodine solutions, following the procedure described by Finley[7] by using a UV–vis spectrophotometer (UV-2401, Shimadzu Co.) The concentration of PVA was kept within $0.02\,\mathrm{g\,L^{-1}}$ and those of boric acid and iodine (dissolved in doubly concentrated potassium iodide) solutions were 12 and $0.76\,\mathrm{g\,L^{-1}}$, respectively. The viscosity of PVA solutions prior to and after irradiation were determined using a Ubblehode meter according to the procedure proposed by Finch.[8] The gaseous products in sealed sample vessels after γ-ray irradiation were determined by using a GC (Model SP-6800A, Lunan Instrument Co.) equipped with a thermal conductivity detector and a 2-m stainless column packed with 5-Å molecular sieves. Argon was used as the carrier gas at a flow rate of $30\,\mathrm{mL\,min^{-1}}$. The structural evolution of PVA prior to and after irradiation was subjected to FTIR (Magna-IR$^{\mathrm{TM}}$ Spectrometer 750, Nicolet Co.) and NMR (AV300, Brucker Co.) analysis. Prior to analysis, the sample solutions were concentrated at reduced pressures and were dried in a vacuum oven at 60 °C. For FTIR analysis, the residues were grounded with KBr powder and were pressed at 40 MPa to form a uniform disk. DMSO-d_6 was used as the solvent for NMR analysis. Chemical shifts were reported as δ referred to DMSO-d_6 as an internal reference.

Irradiation of water with ionizing radiation, e.g., γ rays, leads to the formation of a suite of species, including hydroxyl radicals (•OH), hydrated electrons ($e_{aq}{}^-$), hydrogen atoms (H•), and small amounts of H_2 and H_2O_2. Among these species, •OH and $e_{aq}{}^-$ account together for around 90% of the total radical yield under neutral conditions.[9]

Figure 1 shows the UV–vis absorption spectra of PVA aqueous solutions prior to and after irradiation. With the increase of irradiation dose, an absorption band in the region of about 270 nm was observed. This band was ascribed to $n \rightarrow \pi^*$ transitions of carbonyl groups, substantiating the formation of products with carbonyl groups. On the other hand, the evolution of the absorption spectra of PVA–iodine complex formed prior to and after ir-

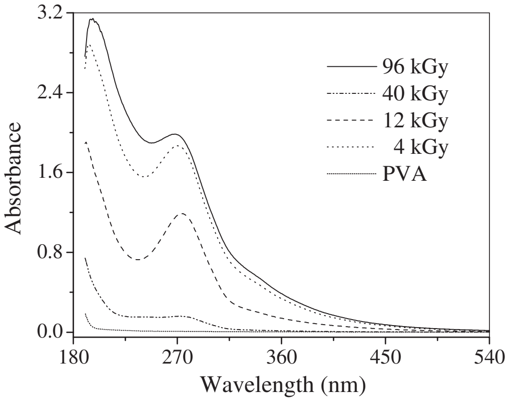

Figure 1. The evolution of UV–vis absorption spectra of PVA aqueous solutions as a function of irradiation dose.

radiation showed that with increasing irradiation dose, the optical density of the PVA–iodine complex reduced significantly, and that the absorption band gradually shifted to shorter wavelength.[5] This shift was attributed to the dependence of the molar extinction coefficient of the PVA–iodine complex on the molecular weight.[10] A sequence of about 120 units of 1, 3-glycol structures is found to be necessary for the formation of the PVA–iodine complex.[8] No PVA–iodine complex could be observed any more after an absorbed dose of 3 kGy, suggesting the scission of PVA main chain.

The relative viscosity (η_r) of PVA aqueous solutions decreased steadily with increasing irradiation dose (data not shown). With the equation between η_r and DP described by Finch,[8] the DP values prior to and after irradiation were calculated. A linear relationship was found between the reciprocal of DP and irradiation dose (r). This suggests that PVA radiolytic degradation followed the random scission mode proposed by Charlesby:[11]

$$1/DP = 1.04 \times 10^{-6}(r + r_0)G$$

where DP is the viscosity-average molecular weight after degradation; r_0 is the "virtual" radiation dose required to fracture an infinitely long chain to give the initial molecular weight distribution; G is the number of main chain scissions per 100 eV of energy absorbed.

Wang et al. observed that irradiation of PVA might result in either crosslinking or degradation of polymer.[12] Contrary to crosslinking, degradation brought about random chain scission and the molecular weight decreased steadily with increasing irradiation dose. The decrease of DP revealed that chain scission predominated in this work.

Hydrogen gas was detected as one of the main gaseous products formed in irradiated PVA aqueous solutions. The H_2 yield of blank solution, i.e., in the absence of PVA, was much lower than that of PVA solution, revealing the role of hydrogen abstraction in the radiolytic degradation of PVA.

The ^{1}H NMR analysis using DMSO-d_6 as solvent provided support for the judgment that hydrogen abstraction was one of the main degradation pathways in PVA radiolysis. As shown in Figure 2, after an absorbed dose of 18 kGy, the signal of H atom in methylene group (β-H) at 1.7 ppm and the signal of H atom α-to OH group at 4.0 ppm both disappeared completely. A further increase in irradiation dose did not result in further evolution in NMR signals, implying that hydrogen-abstracting process was completed. The less abundant signals at 4.3, 4.5, 4.8 ppm derived from the hydrogen atoms in methylidyne groups linked with acetate residues in PVA due to incomplete hydrolysis. New signal of H adjoined to C=O bonds, formed from hydrogen abstraction, was observed in ^{1}H NMR spectra at 2.1 ppm.

FTIR analysis provided a further support for the hydrogen abstraction mechanism. As illustrated in Figure 3, after irradiation a new absorption band at 1707–1712 cm^{-1} appeared, and increased with increasing irradiation dose. This band is the characteristic absorption band of C=O stretching vibration ($\upsilon_{C=O}$). The strong CH_2 bending vibration band at 1423 cm^{-1}, C–H and O–H bending vibration band at 1326 cm^{-1}, strong C–O stretching vibration bands at 1144 cm^{-1} and 1096 cm^{-1}, skeletal vibration bands of PVA at 916 and 849 cm^{-1} all reduced gradually with the increase of irradiation dose, suggesting the destruction of main chain and the formation of products with carbonyl groups.

The formation of hydrogen as the main gaseous product, and the analysis of degradation intermediates by NMR, FTIR, UV–vis, and viscosity determination demonstrated that the mechanism of the radiolytic degradation of PVA was hydrogen abstraction, followed by chain scission.

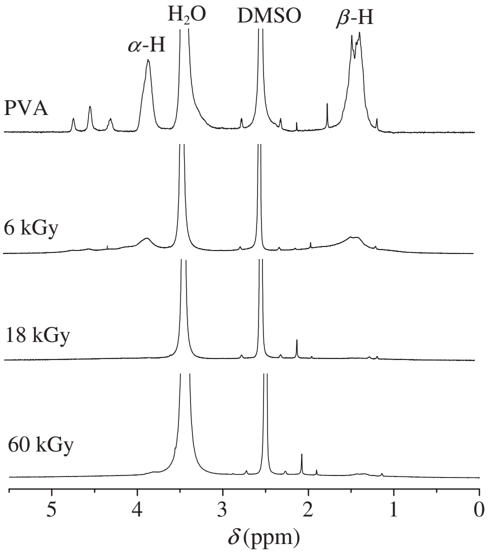

Figure 2. The ^{1}H NMR spectra of PVA and its radiolytic products from irradiated aqueous solutions.

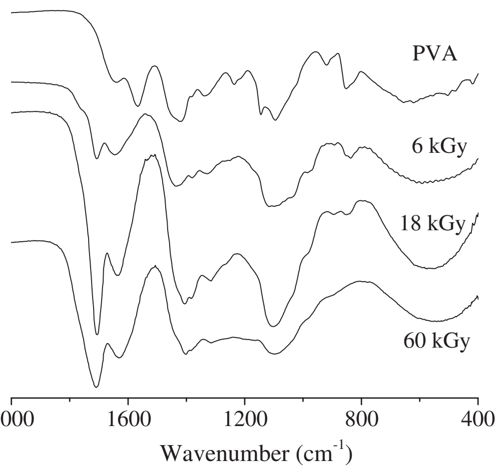

Figure 3. The FTIR spectra of PVA and its radiolytic products from irradiated aqueous solutions.

This work was financially supported by the China Academy of Sciences (CAS) through "The Hundred-Talents Program."

References

1 A. Takasu, H. Itou, M. Takada, Y. Inai, and T. Hirabayashi, *Polymer*, **43**, 227 (2002).
2 B. L. Lopez, A. I. Mejia, and L. Sierra, *Polym. Eng. Sci.*, **39**, 1346 (1999).
3 R. Solaro, A. Corti, and E. Chiellini, *Ploym. Adv. Technol.*, **11**, 873 (2000).
4 A. Sakumoto and T. Miyata, *Radiat. Phys. Chem.*, **24**, 99 (1984).
5 S. J. Zhang and H. Q. Yu, *Water Res.*, **38**, 309 (2004).
6 C. von Sonntag, E. Bothe, P. Ulanski, and D. J. Deeble, *Radiat. Phys. Chem.*, **46**, 527 (1995).
7 J. H. Finley, *Anal. Chem.*, **33**, 1925 (1961).
8 "Polyvinyl Alcohol Properties and Applications," ed. by C. A. Finch, John Wiley & Sons, New York.
9 J. W. Spinks and R. J. Woods, "An Introduction to Radiation Chemistry," 3rd ed., John Wiley & Sons, New York (1990).
10 A. Corti, R. Solaro, and E. Chiellini, *Polym. Degrad. Stab.*, **75**, 447 (2002).
11 "Atomic Radiation and Polymers," ed. by A. Charlesby, Pergamon Press, New York (1960).
12 B. L. Wang, S. Mukataka, E. Kokufuta, and M. Kodama, *Radiat. Phys. Chem.*, **59**, 91 (2000).