Environmental Effects on Latex Paint Coatings. II. CP/MAS ^{13}C-NMR and XPS Investigations of Structural Changes in the Base Polymer

S. S. SANKAR,* D. PATIL,† R. SCHADT,‡ R. E. FORNES,‡ and
R. D. GILBERT,† *Chemistry Department, †Fiber and Polymer
Science Program, ‡Physics Department, North Carolina State
University, Raleigh, North Carolina 27695

Synopsis

Films of a base polymer, primarily a terpolymer of n-butyl acrylate, vinyl acetate, and vinyl chloride, that is used in latex paint, have been exposed to various combinations of UV/air, UV/ SO$_2$, and UV/SO$_2$/H$_2$O. Reported here are results of elemental analyses, XPS and ^{13}C magic angle spinning NMR of the exposed samples. When samples are exposed to UV/SO$_2$ or UV/SO$_2$/H$_2$O, there is clear evidence of the incorporation of sulfur into the polymer, and there is significant loss of the acetate group in the copolymer. There is also evidence of the formation of unsaturated carbon–carbon bonds which is due to loss of the acetate groups and some dehydrohalogenation. During the time scale of exposures, changes in the composition and structure of samples exposed to UV/air were not detected by the techniques considered here although some chain scission and crosslinking undoubtedly occur. The results suggest a synergistic interaction between SO$_2$ and UV leading to rapid degradation of the polymer, and that the presence of atmospheric SO$_2$ pollutants can have an adverse effect on the lifetime of latex coating materials.

INTRODUCTION

In Part I of this investigation,[1] we reported results on the degradative effects of exposure of the base polymer of a latex to combinations of UV, SO$_2$, and H$_2$O. Those investigations included measurements of surface contact angle, sol-gel analysis, intrinsic viscosity of the soluble fraction, and determination of the T_g. It was noted that significant changes occur under short exposure times to the combination of UV/SO$_2$ or UV/SO$_2$/H$_2$O. The data were consistent with both chain scission and crosslinking. Several reaction paths were proposed to account for the change in properties. Here we report measurements made on the same system using cross polarization magic angle spinning ^{13}C-NMR, X-ray Photoelectron Spectroscopy, and elemental analyses to investigate how the polymer is chemically attacked by UV/SO$_2$ or UV/SO$_2$/H$_2$O. Elemental analyses of selected samples are also reported.

EXPERIMENTAL

The copolymer, made using approximately equal molar ratios of n-butyl acrylate (BA), vinyl acetate (VA), and vinyl chloride (VC) with minor amounts of methyl methacrylate (MMA) and acrylic acid (AA) and methacrylic acid

(MAA), was kindly supplied by Union Carbide Corporation. A description of sample preparation and the exposure conditions is given in the previous paper.[1]

When samples were prepared for XPS measurements, special care was taken to avoid contaminating the surfaces of the films. The films were washed with acetone prior to exposure to pollutant gases. Following exposure the films were stored in a vacuum desiccator until XPS measurements were made using a Perkin-Elmer Physical Electronics Industries Model 5400 ESCA system with a concentric hemispherical analyzer. The photoelectrons were excited by Mg K_α X-rays at 400 W power. The system was operated under 10^{-8}–10^{-9} Torr pressure. The diameter of the spot size analyzed was approximately 0.6 mm. Eight samples were placed in the system and analyzed sequentially with a total acquisition time of 4 h (approximately 20/min per sample). The relative abundance of elements C, Cl, O, and S were routinely measured.

Samples were prepared for the NMR measurements from thin films by folding small sections of the exposed films and packing them into the solid state probe. The excess volume was filled with boron nitride to provide stability for the rotor. Some NMR measurements were also done on the soluble and insoluble portions of selected samples. Following extraction of the films with uninhibited THF (Fisher certified) and separation of the fractions, the THF was removed from each fraction by evaporation at approximately 45°C in a vacuum desiccator. The resulting powders were packed into the solid state NMR probe.

Solid state ^{13}C-NMR spectra were obtained at 50.14 MHz on a Chemagnetics 200S NMR spectrometer equipped with a cross polarization magic angle spinning probe (CP-MAS). The rotating field strengths for both the carbons and the protons were approximately 65 kHz. Approximately 5000 transients were collected for all the samples over a spectral width of 15 kHz using 2K data points and a 5.2 μs 90° pulse with a spinning rate of approximately 4.5 kHz. The spectra were obtained with a 2 ms contact time and a pulse delay of 3 s. A sample of paraditertiarybutyl benzene (PDTBB) was used to calibrate the chemical shifts.

The elemental analyses were done by Atlantic Microlab, Atlanta, GA.

RESULTS AND DISCUSSION

Effects on Elemental Composition

Elemental analyses for the control samples and those exposed to UV/air, UV/SO$_2$, and UV/SO$_2$/H$_2$O are given in Table I. No sulfur was detected in the unexposed sample. The C, H, O, and Cl percentages are in reasonable agreement for a copolymer consisting of approximately equimolar amounts of BA, VA, and VC (in this case the weight percents of C/H/O/Cl would be 56.42/7.59/24.10/11.45, respectively) but the results are slightly skewed from this prediction by the presence of a small amount of MMA and very small amounts of AA or MAA. By assuming that the initial composition is based on the following mole percentages: 29% each of BA, VA and VC; 9% of MMA and 4% of AA, the calculated analyses are in quite good agreement with the experimental results for the control samples.

There is little or no change in elemental composition upon exposure to UV/air. However, upon exposure to UV/SO$_2$ or UV/SO$_2$/H$_2$O there is a significant

TABLE I
Elemental Analysis of the Copolymer as a Function of Treatment

Element	Control	UV/air (96 h)	UV/SO$_2$ (96 h)	UV/SO$_2$/H$_2$O (96 h)	Calculated	
					a	b
C	56.44	56.33	44.64	36.85	56.57	45.08
H	7.63	7.81	6.56	6.35	7.57	6.38
O	24.74	24.75	30.89	38.50	24.68	31.97
Cl	11.15	11.10	11.11	9.39	11.18	10.29
S	0.00	0.00	6.32	8.43	0.00	9.27

[a] Based on 29 mol % each butyl acrylate, vinyl acetate, and vinyl chloride; and 9 mol % methyl methacrylate and 4 mol % acrylic acid.

[b] Based on replacing each acetate group with SO$_4$H.

increase in sulfur and oxygen contents with a corresponding decrease in the carbon and hydrogen contents. The chlorine content shows little change.

As noted below, the NMR spectra show clear evidence of loss of the acetate group upon exposure to UV/SO$_2$ or UV/SO$_2$/H$_2$O. By making the simplified assumption that all the acetate groups are replaced by SO$_4$H, the calculated elemental composition is in approximate agreement with the experimental analysis of the UV/SO$_2$ treated samples while the sulfur content is too high (last column, Table I). Obviously, and as shown in Part I, there are a multitude of possible pathways for the reactions between the copolymer and O$_2$, SO$_2$, and/or H$_2$O under the influence of UV light. The relative rates of the various reactions are unknown. Thus it is difficult to predict the composition of the products resulting from the reactions. It is unlikely that all the acetate groups are lost though the NMR results, discussed below, indicate that a majority of these are removed. Surprisingly, in view of the facile dehydrohalogenation of PVC, there only appears to be a relatively small loss of HCl. However, exposure of an unstabilized PVC film to UV/O$_2$/SO$_2$ indicates significant dehydrohalogenation. The marked decrease in the carbon content and corresponding increase in oxygen content on exposure to UV/SO$_2$ and particularly UV/H$_2$O/SO$_2$ strongly suggests acid hydrolysis of the ester groups of the n-butyl acrylate is also occurring. The most important result is the incorporation of sulfur into the polymer when it exposed to UV/SO$_2$ and UV/H$_2$O/SO$_2$.

Shown in Table II is a tabulation of the XPS results on the elements C, O, S, and Cl for samples exposed under various conditions. Also detected were trace amounts of N, Na, and Si, presumably due to surface contamination, and they are not included here. The data are expressed as relative atomic composition per 100 carbon atoms.

The Cl content in the control samples measured by XPS is considerably lower than the results from elemental analysis. It has been shown by Chang and Thomas[2] that Mg K$_\alpha$ X-rays induce significant dehydrohalogenation in PVC, and that the concentration of surface Cl in an XPS measurement decreases monotonically with exposure time. Therefore, the Cl results reported in Table II only serve at best as a qualitative comparison. Samples treated with UV/SO$_2$ and UV/SO$_2$/H$_2$O show a significant reduction of the surface Cl and a significant increase of S compared with the control. The surface S content is comparable to the bulk S content. Samples treated with SO$_2$ only show a small

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TABLE II
ESCA (XPS) Measurements of Relative Atomic Composition (Normalized to Carbon Content)

Sample ID	# of reps.	C	O	S	Cl
Control	3	100	36	0.1	1.6
UV/SO$_2$					
24 h	2	100	47	8.7	0.8
48 h	2	100	36	7.2	0.8
96 h	1	100	28	8.1	0.1
UV/SO$_2$/H$_2$O					
24 h	3	100	39	6.3	0.6
48 h	1	100	61	10	0.4
96 h	2	100	66	12	0.1
UV					
96 h	1	100	40	N/D	1.2
SO$_2$					
96 h	1	100	35	0.3	1.0

buildup of S in the sample indicating that most of the SO$_2$ is quickly removed when the sample is subjected to a vacuum. Hendricks and Balik[3] have shown that this polymer absorbs large amounts of SO$_2$ that is easily removed upon desorption.

The data presented here show there is a synergistic interaction of UV and SO$_2$ resulting in both the incorporation of sulfur into the polymer and that dehydrohalogenation and loss of the acetate groups occur. As shown in Part I,[1] chain scission and crosslinking also occur.

NMR Results

Shown in Figure 1 is the ^{13}C-NMR spectrum of a control sample of the base polymer. Peak assignments are given in Table III and are based on reports in the literature[4-15] and from solid state NMR spectra taken in our laboratory of the homopolymers polyvinyl chloride, polyvinyl acetate, polymethylacrylate,
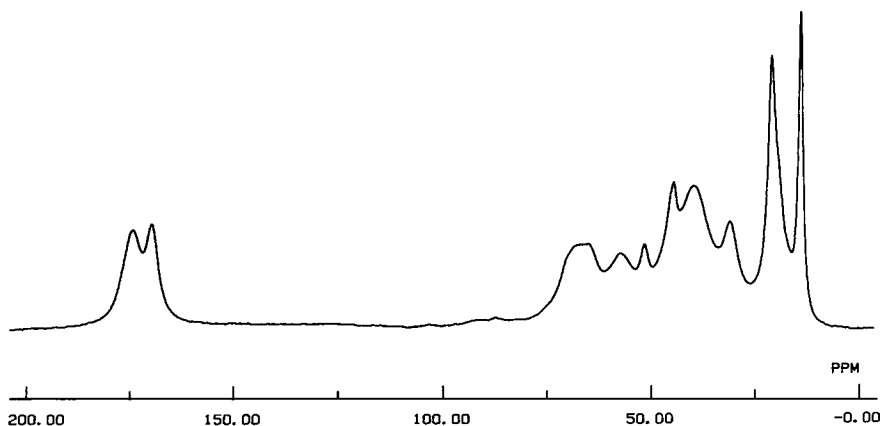

Fig. 1. Solid state ^{13}C-NMR spectrum of the base polymer.

TABLE III
^{13}C Peak Assignments for the Copolymer Containing Mostly Butyl Acrylate (BA), Vinyl Acetate (VA), and Vinyl Chloride (VC) Units and Some Methyl Methacrylate (MMA)

Chemical shift	Carbon type	Structural unit assigned
13.5	—CH$_3$	BA
18–19	R—C—CH$_3$, —CH$_2$—CH$_3$	MMA, BA
20.5	—CH$_3$	VA
30.6	—O—CH$_2$—CH$_2$—CH$_2$—CH$_3$	BA
35–36	—CH$_2$—CH—	BA
39	—CH$_2$—CH—	VA
41	—CH$_2$—CH—	BA
44–45	—CH$_2$—CH—, —CH$_2$—C—	VC, MMA
51.3	—C—O—CH$_3$, —CH$_2$—C—	MMA
56.9	—CH$_2$—CH—	VC
64.4	—C—O—CH$_2$—	BA
68.7	—CH$_2$—CH—OCCH$_3$	VA
169.7	—C—O—	VA
174.4	—C—O—	BA, MMA

and polymethylmethacrylate. Polybutyl acrylate is liquid at room temperature; its high resolution spectrum is shown in Figure 2.

Shown in Figures 3–5 are the ^{13}C spectra of samples exposed for 96 h to UV, UV/SO$_2$, and UV/SO$_2$/H$_2$O, respectively. The spectra of films exposed to UV (or SO$_2$ which is not shown here) alone are essentially identical to the control.

However, there are several marked changes in spectra of samples exposed to UV/SO$_2$ and UV/SO$_2$/H$_2$O compared with that of the control. The peak around 170 ppm associated with the carbonyls of the vinyl acetate units is
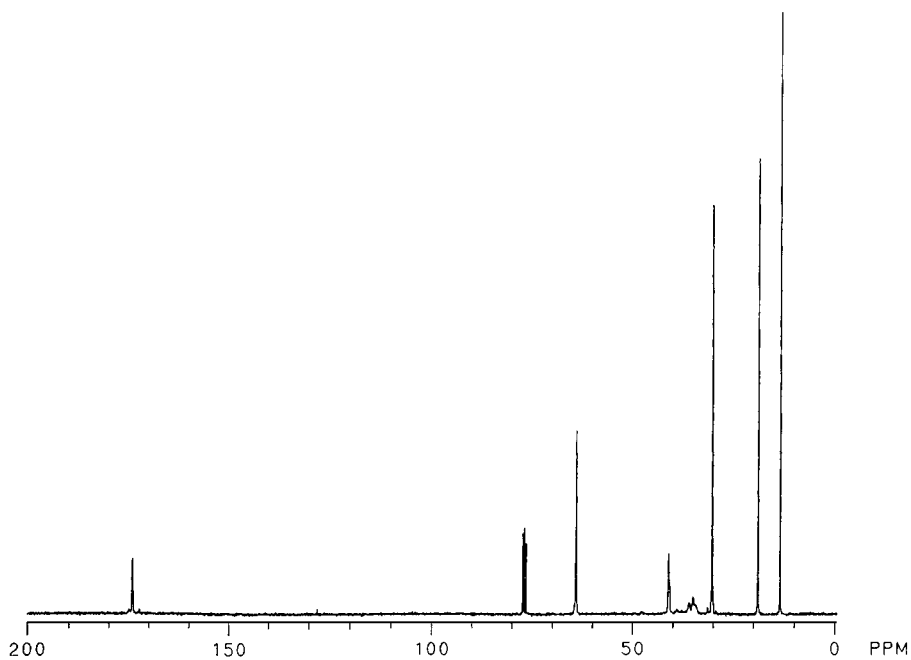
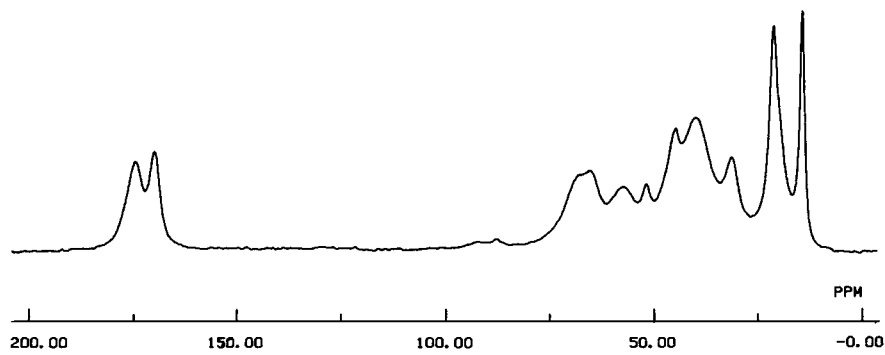Fig. 2.   High resolution ^{13}C-NMR spectrum of polybutyl acrylate in CDCl$_3$.

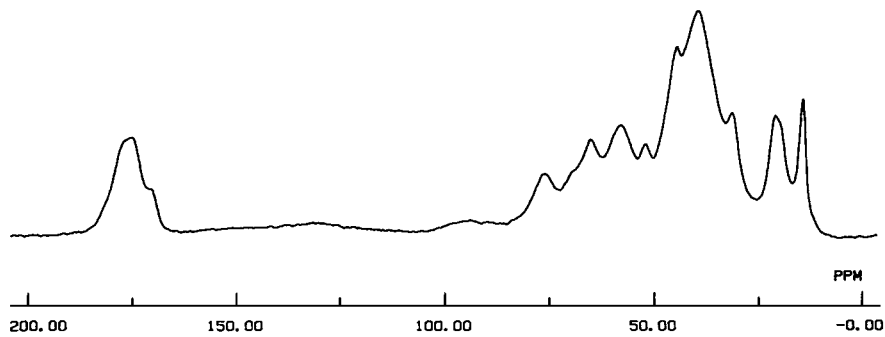Fig. 3.   Solid state ^{13}C-NMR spectrum of the base polymer exposed to UV for 96 h.

Fig. 4.   Solid state ^{13}C-NMR spectrum of the base polymer exposed to UV/SO$_2$ for 96 h.
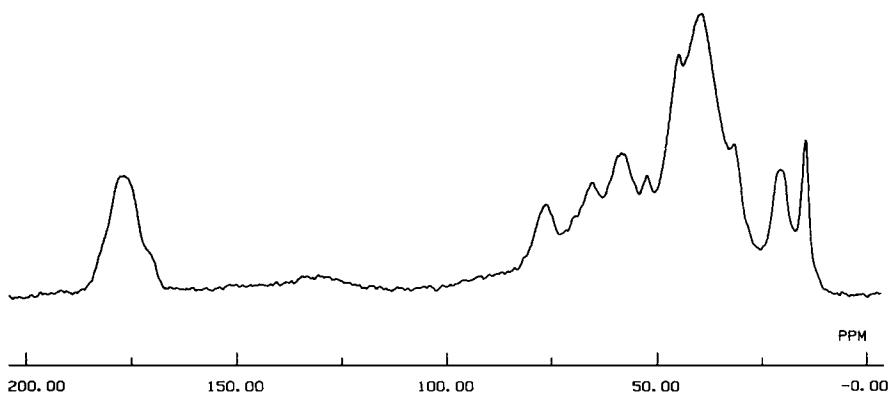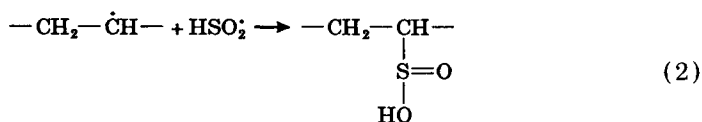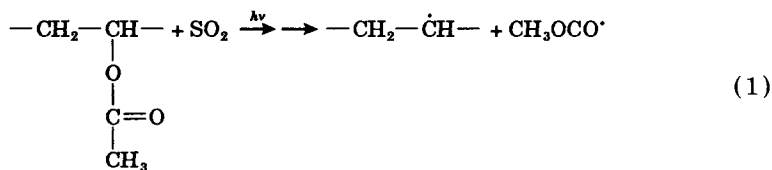
Fig. 5. Solid state ^{13}C-NMR spectrum of the base polymer exposed to $UV/SO_2/H_2O$ for 96 h.

reduced significantly upon exposure. There is also depletion of the peak around 68 ppm which is assigned to the methine carbons of the vinyl acetate units. However, the intensity of the peak ca. 39 ppm, assigned to the methylene carbon of the vinyl acetate unit, did not decrease as expected. Two possible explanations are: the peak at ca. 39 ppm in the spectrum of the exposed sample (Figs. 4 and 5) could include a number of peaks including that ca. 36 and 41 ppm corresponding to the methylene and methine carbons of the butyl acrylate unit; and/or upon the loss of the acetate group, there is a fast reaction with SO_2. There is a peak of relatively high intensity ca. 76 ppm in the spectra of the polymer after exposure to UV/SO_2 or $UV/SO_2/H_2O$. This could possibly be accounted for by the formation of sulfinic acid. Dainton and Ivin[18] showed sulfinic acids are formed when hydrocarbons are exposed to UV and SO_2. The C-1 carbon of 2,2-dimethyl propane sulfinic acid has been reported to resonate at 72 ppm, the C-2 at 30.1 ppm and the C-3 at 29.9 ppm.[16] The methylene carbon adjacent to the methine carbon attached to the SO_2H probably resonates near the 31 ppm region and could well be under the peak centered at 39 ppm. A possible reaction scheme is shown below.

$$-CH_2-\underset{\underset{\underset{CH_3}{|}}{\overset{\overset{O}{|}}{\underset{|}{C=O}}}{CH}- + SO_2 \xrightarrow{h\nu} \longrightarrow -CH_2-\dot{C}H- + CH_3OCO^{\boldsymbol{\cdot}} \qquad (1)$$

$$-CH_2-\dot{C}H- + HSO_2^{\boldsymbol{\cdot}} \longrightarrow -CH_2-\underset{\underset{HO}{|}}{\overset{\overset{}{|}}{\underset{|}{S=O}}}{CH}- \qquad (2)$$

There is a broad peak around 135 ppm in the spectra of the UV/SO_2 and $UV/SO_2/H_2O$ treated samples that does not appear in the other samples. This peak is consistent with the formation of unsaturated carbon-carbon bonds formed by either dehydrohalogenation or loss of acetic acid. Shown in Figures 6 and 7 are the spectra of a control sample of PVC and one exposed to UV/SO_2, the latter of which clearly shows the presence of the 135 ppm peak. Pure PVA exposed to UV/SO_2 for comparable periods also show the broad peak at 135 ppm. Since NMR
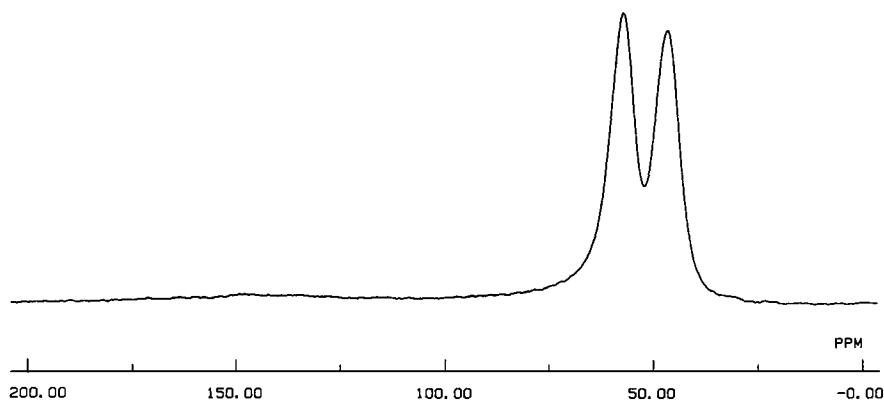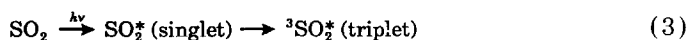
Fig. 6. Solid state ^{13}C-NMR spectrum of poly(vinyl chloride).

measures bulk properties, these results suggest that in the presence of UV/SO$_2$ the polymer is attacked throughout the thickness of the film and not just at the surface. These data are also consistent with the elemental analysis results discussed above. The chemical moiety causing the peak ca. 135 ppm accounts for the rapid discoloration of the films upon exposure.
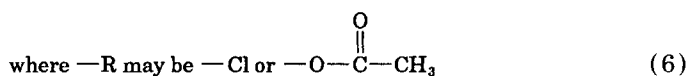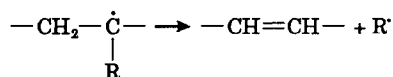
With the large increase in the amount of S in the samples exposed in the presence of UV/SO$_2$ or UV/SO$_2$/H$_2$O, it is speculated that carbon–sulfur bonds may form along the lines suggested by others. Jellinek[17] proposed the following reaction paths:
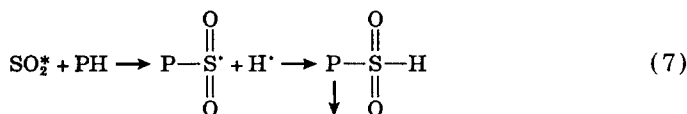
$$SO_2 \xrightarrow{h\nu} SO_2^* \text{ (singlet)} \longrightarrow {}^3SO_2^* \text{ (triplet)} \tag{3}$$

$$PH + SO_2^* \longrightarrow PSO_2H \tag{4}$$

or the following:

$$PH + SO_2 \xrightarrow{h\nu} P^{\cdot} + HSO_2^{\cdot} \tag{5}$$

Expressing P$^{\bullet}$ in (5) as

$$-CH_2-\overset{\cdot}{\underset{\underset{R}{|}}{C}}- \longrightarrow -CH{=}CH- + R^{\cdot}$$

$$\text{where } -R \text{ may be } -Cl \text{ or } -O-\overset{\overset{\textstyle O}{\|}}{C}-CH_3 \tag{6}$$

Dainton and Ivin[18] also suggested photoactivated reactions in polymers produce sulfinic acids:

$$SO_2^* + PH \longrightarrow P-\overset{\overset{\textstyle O}{\|}}{\underset{\underset{\textstyle O}{\|}}{S}}{}^{\cdot} + H^{\cdot} \longrightarrow P-\overset{\overset{\textstyle O}{\|}}{\underset{\underset{\textstyle O}{\|}}{S}}-H \tag{7}$$

$$P-\underset{\underset{\textstyle O}{\|}}{S}-OH \tag{8}$$

The combined reaction schemes (3)–(8) also accounts for the increase in the
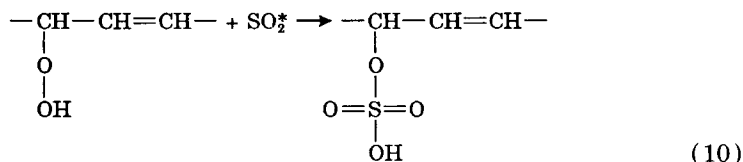
135 ppm peak, the rapid discoloration in the films, and the increase in the S content and loss of Cl from the sample. If R in (6) is the acetate group, then that reaction could account for the loss of the 170 ppm and 68 ppm peaks. It is noted that the samples exposed to UV/SO_2 or $UV/SO_2/H_2O$ emit an odor characteristic of acetic acid, a result also consistent with the loss of the acetate groups.

In Part I of this work,[1] we proposed that the presence of O_2 can lead to the following products from a chain scission reaction:

$$-CH_2-\overset{\overset{O}{\|}}{C}-\dot{C}H_2 + R-CH=CH- + H^{\cdot} \qquad (9)$$
$$\text{I}$$
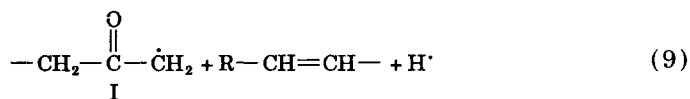
Product I in (9) can combine with $HSO_2^{\bullet}$ or SO_2^{*} to incorporate S into the polymer network. The reactions leading to (9) also involve the elimination of a side group which is consistent with the loss of acetate groups and dehydrohalogenation.

It should be noted, however, that the chemical shift associated with sulfides (C-S-R), sulfoxides (C-SO-R), and sulfones (C-SO_2-R) are usually reported in the range of 30–60 ppm.[19-20] We also speculated in Part I that in the presence of O_2 hydroperoxides would be formed and that SO_2 may further react with them. Gesner[21] and Davies[22] have suggested the latter type reaction. Thus we could have

$$-\underset{\underset{OH}{\overset{|}{O}}}{\overset{|}{C}}H-CH=CH- + SO_2^{*} \longrightarrow -\underset{\underset{\underset{OH}{\overset{|}{O=S=O}}}{\overset{|}{O}}}{\overset{|}{C}}H-CH=CH- \qquad (10)$$

The chemical shift in methine adjacent to the SO_4H group would be shifted down field compared with the carbons adjacent to the sulfinic acid group or the carbon adjacent to the sulfur in sulfides or sulfones. Therefore, the reaction product in (10) could account for the peak ca. 76 ppm. The dramatic increase in the uptake of sulfur and oxygen when H_2O is present lends support to the reaction scheme proposed in (10).
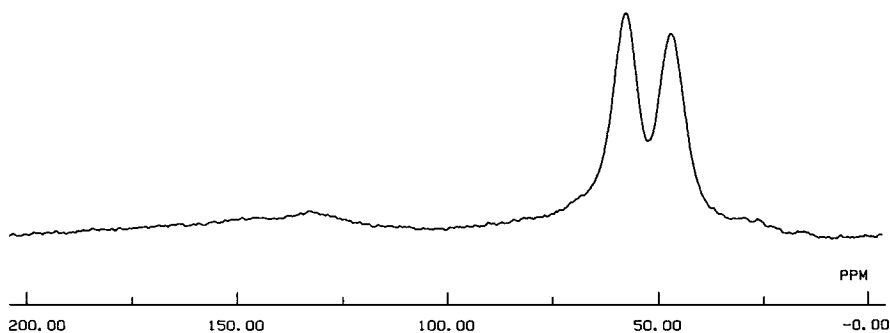

PPM

| 200. 00 | 150. 00 | 100. 00 | 50. 00 | -0. 00 |

Fig. 7.   Solid state ^{13}C-NMR spectrum of poly(vinyl chloride) exposed to $UV/SO_2/H_2O$ for 96 h.

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