A Study Using ^{13}C CP/MAS NMR of Microstructural Changes in Acrylate Copolymers Due to Photolytic/SO$_2$ Degradation

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SYNOPSIS

Photolytic degradation (350 nm) of acrylate-type copolymer films in the presence of SO$_2$ and H$_2$O has been examined using ^{13}C CP/MAS NMR. Copolymers in this study are used as binders in the paint and adhesives industry. The compositions contain butyl acrylate, vinyl acetate, vinyl chloride, and methyl methacrylate units in various combinations. Elemental analyses of the samples allow comparisons and confirmations of structural changes observed in the NMR spectra. A significant result is identification of pendant sulfate group incorporation in UV/SO$_2$ or UV/SO$_2$/H$_2$O-exposed VAc/BA-type copolymers which has been attributed to a co-unit interaction between BA and VAc units. It is suggested that effects on T_g, the glass transition temperature, may account in part for this co-unit effect on photodegradation.

INTRODUCTION

Exposure of polymers to hostile environments can produce a host of changes in the polymer microstructure and physical properties including chain scission, crosslinking, embrittlement, discoloration, and substituent loss.[1-3] It was previously reported[2] that, on exposure to UV/SO$_2$ or UV/SO$_2$/H$_2$O, an acrylate-type copolymer [primarily consisting of equimolar amounts of butyl acrylate (BA), vinyl acetate (VAc), and vinyl chloride (VC) units, and a minor amount of methyl methacrylate (MMA) units] exhibited dehydrochlorination, loss of acetate groups, and sulfur incorporation. The incorporation of sulfur was ascribed to the formation of sulfinic acid and/or sulfate groups.[2]

Here we report evidence to support incorporation of sulfate groups due to UV/SO$_2$ or UV/SO$_2$/H$_2$O exposure. A co-unit effect of butyl acrylate units, primarily between VAc and BA structural units, occurs and may be responsible for the observed loss of substituents and sulfur incorporation.

EXPERIMENTAL

Experimental procedures are described elsewhere in detail.[1-3] Copolymers were kindly supplied by Union Carbide (primarily BA/VAc/VC with a small amount of MMA), Rohm and Haas (MMA/BA), B. F. Goodrich (VC/BA), Unocal (VAc/BA), and Polysciences (VC/VAc). The approximate molar composition of each copolymer is given in Table III. Thin uniform films (ca. 127 μm) were cast on release paper, dried for 2 h at room temperature, separated from the paper, dried under vacuum for 48 h at 40°C, and stored under N$_2$ in a desiccator until use. The films were exposed, in a Rayonet RPR-100 photochemical reactor, to combinations of UV (350 nm), SO$_2$, air, and H$_2$O at ca. 40°C in quartz tubes fitted with inlet and outlet tubes. After exposure, films were dried under vacuum for 48 h at 40°C and then cut and packed into the solid-state NMR rotor. Excess volume in the rotor was filled with boron nitride in order to provide spinning stability. Solid state ^{13}C NMR spectra were obtained at 25.18 MHz on an IBM 100 MHz spectrometer equipped with a CP/MAS probe. Rotating field strengths for both carbons and protons were ca. 60 kHz. Approximately 2000–5000 transients were collected for each spec-

trum over a spectral width of 15 kHz using 2K data points, a 6 μs 90° pulse, and a spinning frequency of 2 kHz. Spectra were obtained with a 2 ms contact time and a pulse delay of 3 s. Chemical shifts were calibrated with paraditertiarybutyl benzene. Elemental analyses were provided by Atlantic Microlab and the Schwarzkopf Microanalytical Laboratory. XPS (X-ray photoelectron spectroscopy) spectra were measured in the Chemistry Department, UNC-Chapel Hill.

RESULTS AND DISCUSSION

The ^{13}C CP/MAS NMR spectrum of the copolymer consisting of approximately equimolar amounts of BA, VAc, and VC, with a minor amount of MMA (referred to below as BA/VAc/VC) is in Figure 1.

Peak assignments (Table I) are based on literature values and/or solid-state NMR spectra obtained in our laboratory for PVC, PVAc, PMMA, PBA, and copolymers of MMA/BA, VC/BA, VC/VAc, and VAc/BA. Complete assignments of each chemical shift for each copolymer in this study are given elsewhere.[3] Spectra of the copolymers exposed for 96 h to UV or SO_2 alone (not shown here) are nearly identical to their respective unexposed counterparts.[2,3] On the other hand, the spectra of the copolymers exposed for 96 h to UV/SO_2 (or UV/SO_2/H_2O) show significant changes. For example, the ^{13}C NMR spectrum of the 96 h UV/SO_2-exposed BA/VAc/VC copolymer exhibits a peak at ca. 76 ppm which is not present in the unexposed copolymer spectrum (Fig. 1). The intensity of this peak increases with exposure duration and SO_2 concentration.[3] Formation of sulfate groups has been pre-
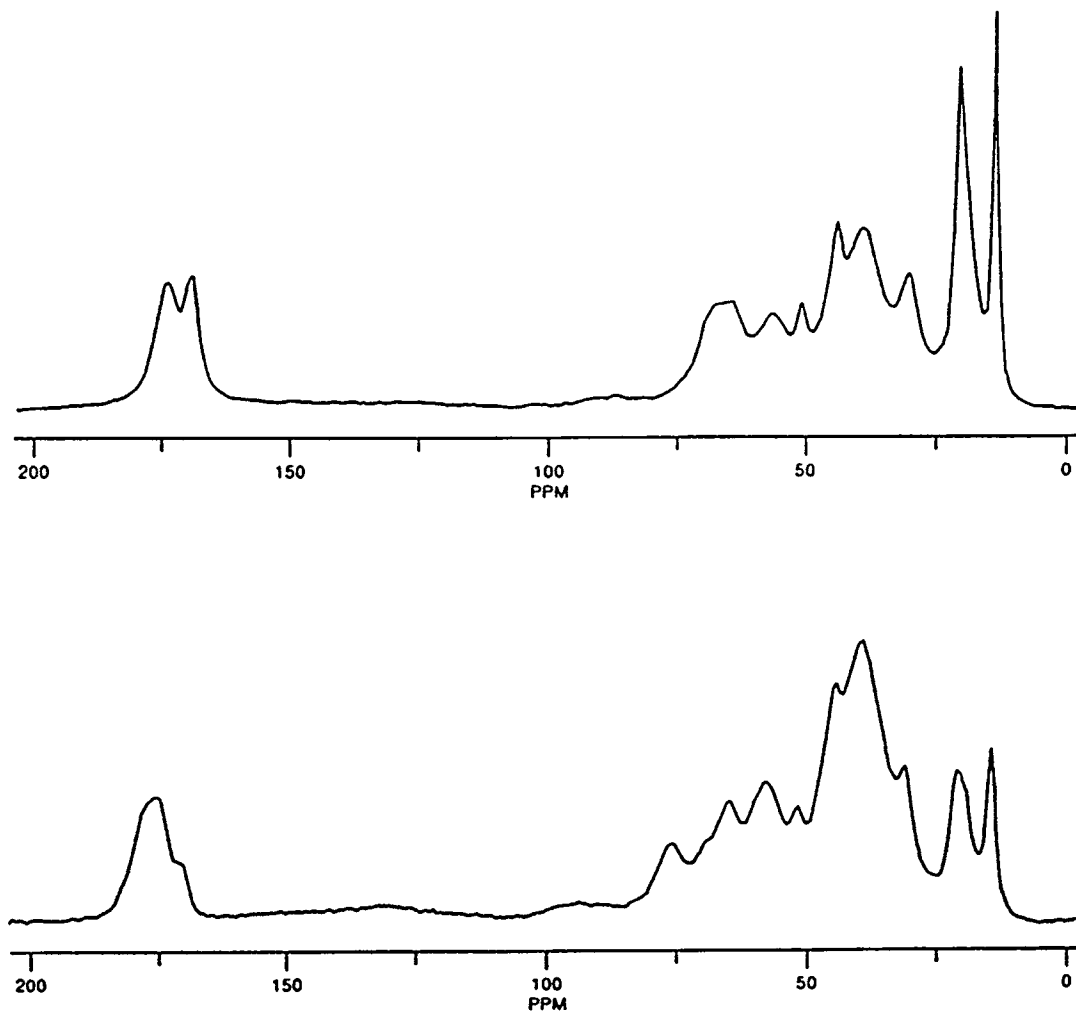
Figure 1 ^{13}C CP/MAS NMR of: (a) BA/VAc/VC copolymer (top); (b) BA/VAc/VC copolymer after UV/SO_2 96 h exposure (bottom).

Table I ^{13}C CP/MAS NMR Peak Assignments[2,3] (Error is ±0.1 ppm)

| Chemical Shift (ppm)	Carbon Type	Structural Unit Assigned
13.5	—$\underline{C}H_3$	BA
18–19	$R—\overset{\mid}{\underset{\mid}{C}}—\underline{C}H_3, \ —\underline{C}H_2—CH_3$	MMA, BA
20	—$\underline{C}H_3$	VAc
30.6	—O—CH_2—$\underline{C}H_2$—CH_2—CH_3	BA
35–36	—$\underline{C}H_2$—$\underset{\mid}{CH}$—	BA
39	—$\underline{C}H_2$—$\underset{\mid}{CH}$—	VAc
41	—CH_2—$\underset{\mid}{\underline{C}H}$—	BA
44–45	—$\underline{C}H_2$—$\underset{\mid}{CH}$—, —CH_2—$\overset{\mid}{\underset{\mid}{\underline{C}}}$—	VC, MMA
51.3	$\overset{O}{\overset{\|}{—C}}$—O—$\underline{C}H_3$, —$CH_2$—$\overset{\mid}{\underset{\mid}{\underline{C}}}$—	MMA
56	—CH_2—$\underset{\mid}{\underline{C}H}$—	VC
64	$\overset{O}{\overset{\|}{—C}}$—O—$\underline{C}H_2$—	BA
68	—CH_2—$\underset{\mid}{\underline{C}H}$—$\overset{O}{\overset{\|}{OC}}CH_3$	VAc
169.7	$\overset{O}{\overset{\|}{—\underline{C}}}$—O—	VAc
174	$\overset{O}{\overset{\|}{—\underline{C}}}$—O—	BA, MMA

viously observed in other polymers such as polystyrene, polysulfone, and polypropylene[4-7] which were exposed to UV and SO_2. For chemical shift comparison, the ^{13}C CP/MAS NMR spectrum of poly(vinyl sulfate) (K salt) (PVS) is shown in Figure 2. The chemical shift at ca. 76 ppm has been assigned to the methine carbon attached to a sulfate group.[2,3]

Elemental analyses (Tables II and III) of the copolymers show significant increases in sulfur content after UV/SO_2 or UV/SO_2/H_2O exposure. There is no change in S content on exposure to only SO_2 or SO_2/H_2O.[1-3] This result is consistent with the observation that the SO_2-exposed BA/VAc/VC co-

polymer absorbs SO_2, but subsequently desorbs virtually all the SO_2 under vacuum.[8] As the samples in this study were dried under vacuum after exposure, the observed S concentration in the UV/SO_2 or UV/SO_2/H_2O-exposed samples is principally due to S incorporation onto the polymer backbone which occurs in the presence of UV and SO_2.

Sample composition calculations (BA/VAc/VC copolymer), based on the assumption that all VAc pendant groups are replaced by —SO_4H (sulfate groups) or —SO_2H (sulfone or sulfinic acid groups), indicate closer agreement for sulfate group incorporation (Table II), and suggest —SO_4H group incorporation dominates over incorporation of sulfinic
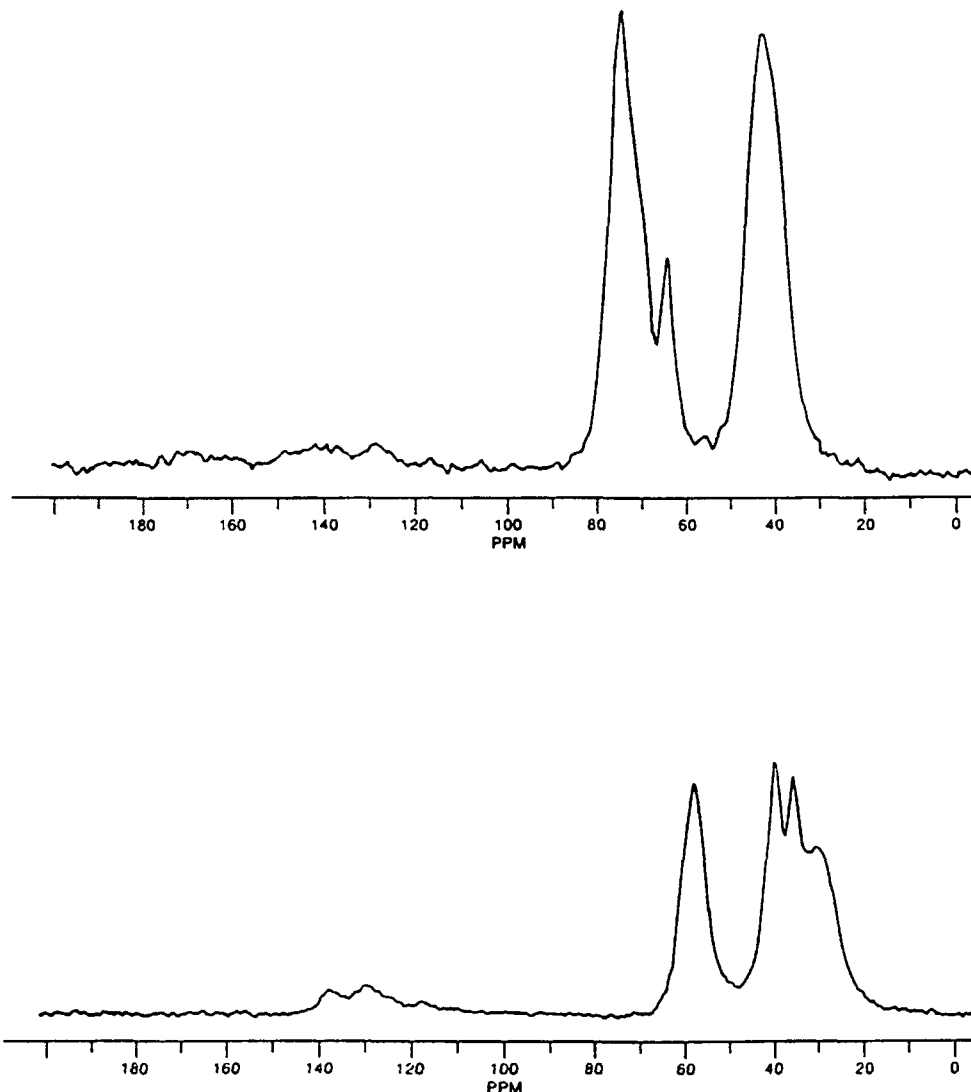
Figure 2 ¹³C CP/MAS NMR of: (a) polyvinyl sulfate (K salt) (top); (b) polymethyl vinyl sulfone (bottom).

acid groups. In addition, XPS (Fig. 3) clearly shows an S 2p binding energy peak at ca. 169.5 eV assigned to sulfate groups[3,9,10] and a small peak at ca. 164 eV due to C—S bonds[3,10] (possibly sulfone groups) in the UV/SO₂ (or UV/SO₂/H₂O)-exposed BA/VAc/VC copolymer which are not present in the XPS spectra of the unexposed copolymer.[3] Integration of the NMR peak at ca. 76 ppm for UV/SO₂ (Fig. 1) or UV/SO₂/H₂O (96 h) exposures of the BA/VAc/VC copolymer gives C—S percentages consistent with S elemental analysis, but does not completely account for all of the increase in S content.[3] Part of the S increase may correspond to observed intensity increases in the 30–60 ppm range (Fig. 1) which may be associated with carbon environments in

other C—S type species, e.g., sulfones (C—SO₂—R). For comparison, the ¹³C NMR spectrum of polymethyl vinyl sulfone (PMVS) (Fig. 2) shows a chemical shift at ca. 35 ppm assigned to the —CH₂— group, and a shift at ca. 58 ppm is assigned to the methine carbon.[3] However, the ¹³C NMR spectrum of poly(vinyl sulfate) (PVS) (K salt) (Fig. 2) clearly shows a chemical shift at ca. 40 ppm, assigned to the —CH₂— group,[3] suggesting the observed intensity increases in the 40 ppm region are a consequence of incorporation of sulfate groups.

The experimental evidence strongly indicates the signal at 76 ppm is due to incorporation of sulfate groups. The same peak also appears in the spectrum of the VAc/BA copolymer after exposure to UV/

Table II   Elemental Analysis of UV/SO$_2$-Exposed BA/VAc/VC Copolymer (Including Concentration Calculations)[a]

Copolymer	UV/SO$_2$ (96 h)	Element Concentration (%)				
		C	H	Cl	O	S
BA/VAc/VC[1]	—	56.44	7.63	11.15	24.74	0
BA/VAc/VC[2,3]	Yes	44.64	6.56	11.11	30.89	6.32
		Calculated Values				
1[b]		56.57	7.57	11.18	24.68	0
2[c]		43.77	6.20	9.99	31.04	9.00
3[d]		48.10	6.81	10.97	24.22	9.89

[a] Error is ±0.1 for each concentration.
[b] Based on 29 molar % of BA, VAc, and VC; and 9 molar % of MMA and 4 molar % of acrylic acid.
[c] Based on replacing each VAc pendant group with —SO$_4$H.
[d] Based on replacing each VAc pendant group with —SO$_2$H.

**Table III   Elemental Analysis of Polymers in Co-Unit Effect Study (UV/SO$_2$-Type Exposures)[a]**

Sample	UV/SO$_2$ (96 h)	Element Concentration (%)				
		C	H	Cl	O	S
PVAc	—	55.27	7.15	—	37.58	0
	—	55.8	6.98	—	37.21	0[d]
	Yes	51.70	7.14	—	39.31	1.85
PBA	—	65.81	9.50	—	24.69	0
	—	65.63	9.38	—	25.00	0[d]
	[c]	54.47	8.75	—	32.86	3.92
VC/VAc	—	43.33	5.57	39.97	11.13	0
75%/25%	—	43.88	5.48	38.94	11.70	0[d]
	Yes	41.51	5.34	38.34	12.40	2.41
MMA/BA	—	61.87	9.01	—	28.44	0.40
60%/40%	—	62.59	8.63	—	28.78	0[d]
	Yes	51.93	8.18	—	34.24	5.02
BA/VAc/VC[b]	—	56.44	7.63	11.15	24.74	0
29%/29%/29%	—	56.57	7.57	11.18	24.68	0[d]
	[d]	43.96	6.82	11.35	32.80	5.07
	Yes	44.64	6.56	11.11	30.89	6.32
VAc/BA	—	57.75	7.67	—	34.58	0
81.7%/18.3%	—	58.27	7.58	—	34.16	0[d]
	Yes	45.88	7.11	—	39.85	7.16
VC/BA	—	53.33	7.54	22.89	16.24	0
55%/45%	—	55.45	7.67	21.23	15.66	0[d]
	Yes	43.17	6.28	17.95	25.38	7.22

[a] Calculated molar composition (%) which approximately agrees with the measured elemental concentrations of each unexposed polymer are included. Error is ±0.1 for each concentration.
[b] Contains minor amounts of MMA and acrylic or methacrylic acid. See Table II.
[c] UV/SO$_2$ 48 h exposure.
[d] Calculated values.
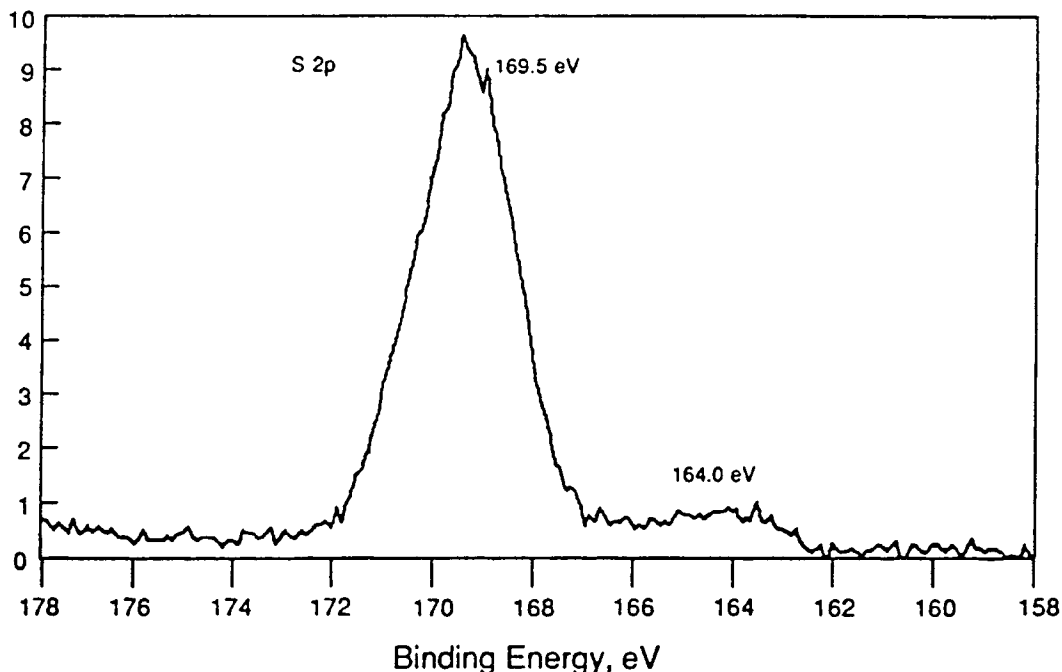
Figure 3 XPS S elemental scan of BA/VAc/VC copolymer after UV/SO_2 96 h exposure. The 169.5 eV peak is assigned to sulfate groups.

SO_2 (or UV/SO_2/H_2O) (Fig. 4). The signal at ca. 76 ppm does not clearly appear in the ^{13}C NMR spectra of the other copolymers reported here. This result implies a co-unit effect between BA units and VAc units was operating during degradation.

Another important observation is that a broad peak which develops around 130 ppm (Fig. 1) can be associated with formation of polyenes due to loss of acetate groups or chlorine.[2,3] The ^{13}C NMR spectrum of UV/SO_2-exposed (96 h) PVC shows formation of a broad peak near 130 ppm.[2] The presence of a peak at ca. 130 ppm generally coincides with darkening (all the unexposed films in this study are transparent) of the polymer films upon UV/SO_2 or UV/SO_2/H_2O exposure.[3]

Surprisingly, the spectrum of polyvinyl acetate (PVAc) after exposure to UV/SO_2 is similar to that of the unexposed polymer (Fig. 5). This observation, in view of the marked structural changes in the BA/VAc/VC copolymer,[2,3] also suggests that a VAc/BA co-unit effect was operating. Copolymers of VAc/BA, MMA/BA, VC/BA, and VC/VAc were exposed to UV/SO_2 (or UV/SO_2/H_2O) for 96 h and their ^{13}C NMR spectra collected within 1 week after exposure to limit any structural changes on storage (the ester —CH_3 signal of the BA/VAc/VC copolymer decreased when an exposed sample was stored at room temperature for 2 months.[3]

The elemental analyses of the UV/SO_2-exposed VC/BA copolymer show a significant increase in sulfur and oxygen content and a decrease in carbon content (Table III). The ^{13}C NMR spectra (Fig. 6) show a decrease in the —CH_3 signal attributed to the butyl ester group. The loss of butoxide side groups by scission of the butyl ester linkage could account for the decrease in the —CH_3 signal and the decrease in carbon content. There is also an increase in the intensity of the signals in the 30–60 ppm region which has been attributed to carbons attached to sulfoxide or sulfone groups.[3]

Similarly, the MMA/BA copolymer has increases in sulfur and oxygen content and a decrease in carbon content on exposure to UV/SO_2 (Table III). The ^{13}C NMR spectra (Fig. 7) show changes similar to the VC/BA copolymer after exposure. However, the carbonyl signal is significantly decreased for the MMA/BA copolymer after exposure.

The VAc/BA copolymer after UV/SO_2 exposure has significantly increased levels of sulfur and oxygen and a lower carbon content (Table III). The ^{13}C NMR spectra (Fig. 4) show increases in the intensity of the signals in the 30–50 ppm region (due to sulfone formation), an increase in intensity of the signal at ca. 70 ppm possibly due to sulfinic acid formation, and the appearance of the signal at ca. 76 ppm attributed to sulfate formation. There is a
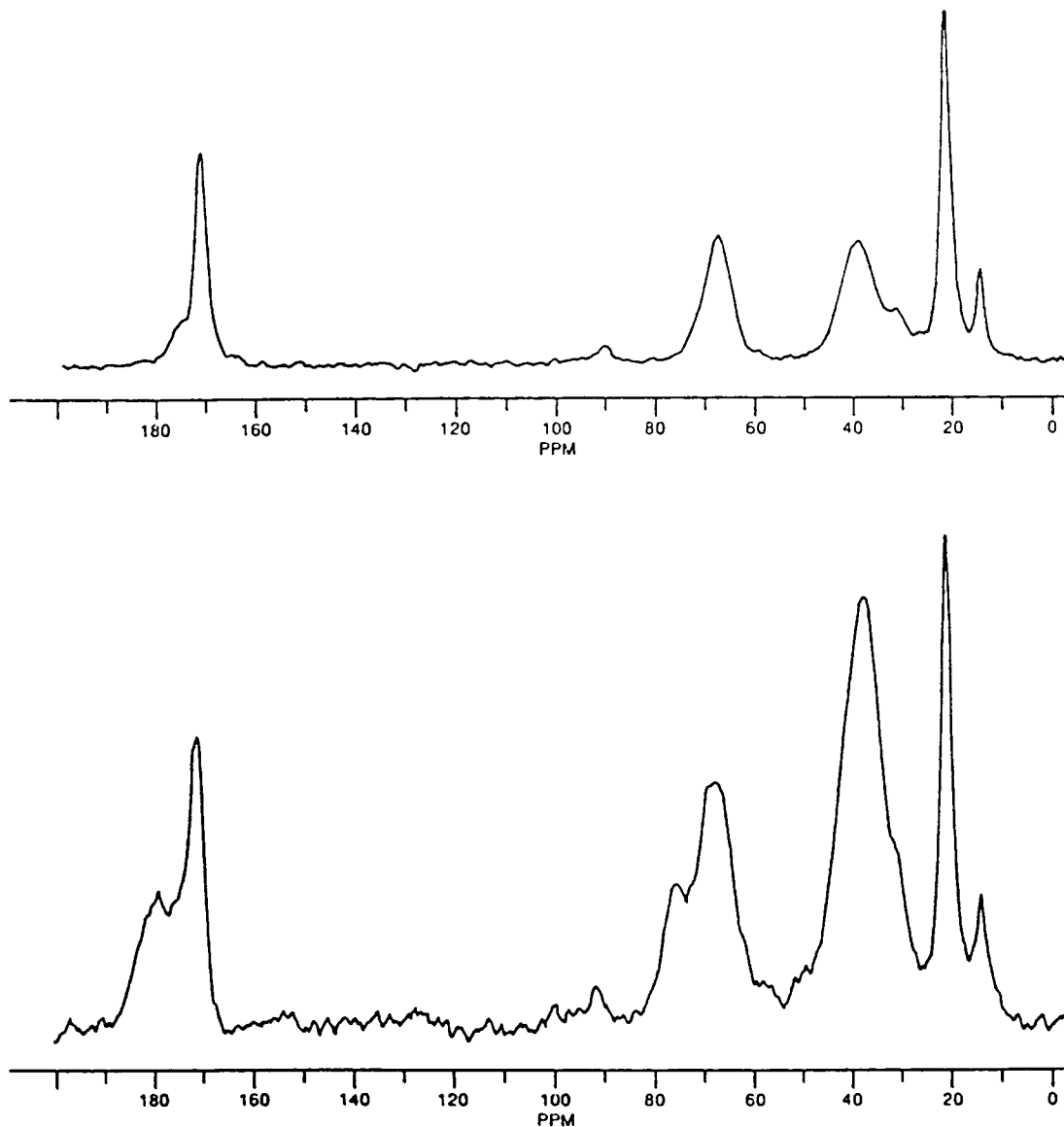
Figure 4 ^{13}C CP/MAS NMR of: (a) VAc/BA copolymer (top); (b) VAc/BA copolymer after UV/SO$_2$ 96 h exposure (bottom).

pronounced peak at 180 ppm which could be due to the presence of acetic acid resulting from acetate group removal, or possibly due to the formation of butyraldehyde from BA pendant groups.[3]

Compared to the copolymers containing BA, the VC/VAc copolymer has a much smaller increase in sulfur and oxygen content and a smaller decrease in carbon content after UV/SO$_2$ exposure (Table III). The ^{13}C NMR spectrum of the exposed copolymer is virtually identical to that of the unexposed sample (Fig. 8).

Polybutyl acrylate (PBA) also has increased levels of sulfur and oxygen and a decreased carbon con-

tent after UV/SO$_2$ exposure (Table III). The ^{13}C NMR spectrum (not shown) of PBA after exposure is similar to that of the unexposed sample.

PVAc, which as noted above has similar ^{13}C NMR spectra before and after UV/SO$_2$ exposure (Fig. 5), does have small increases in the levels of sulfur and oxygen and a small decrease in carbon content (Table III).

Summarizing these observations, PVAc and PBA show only relatively small structural changes upon exposure to UV/SO$_2$ (or UV/SO$_2$/H$_2$O). However, if BA units are present in a copolymer, marked structural changes and sulfur incorporation as either
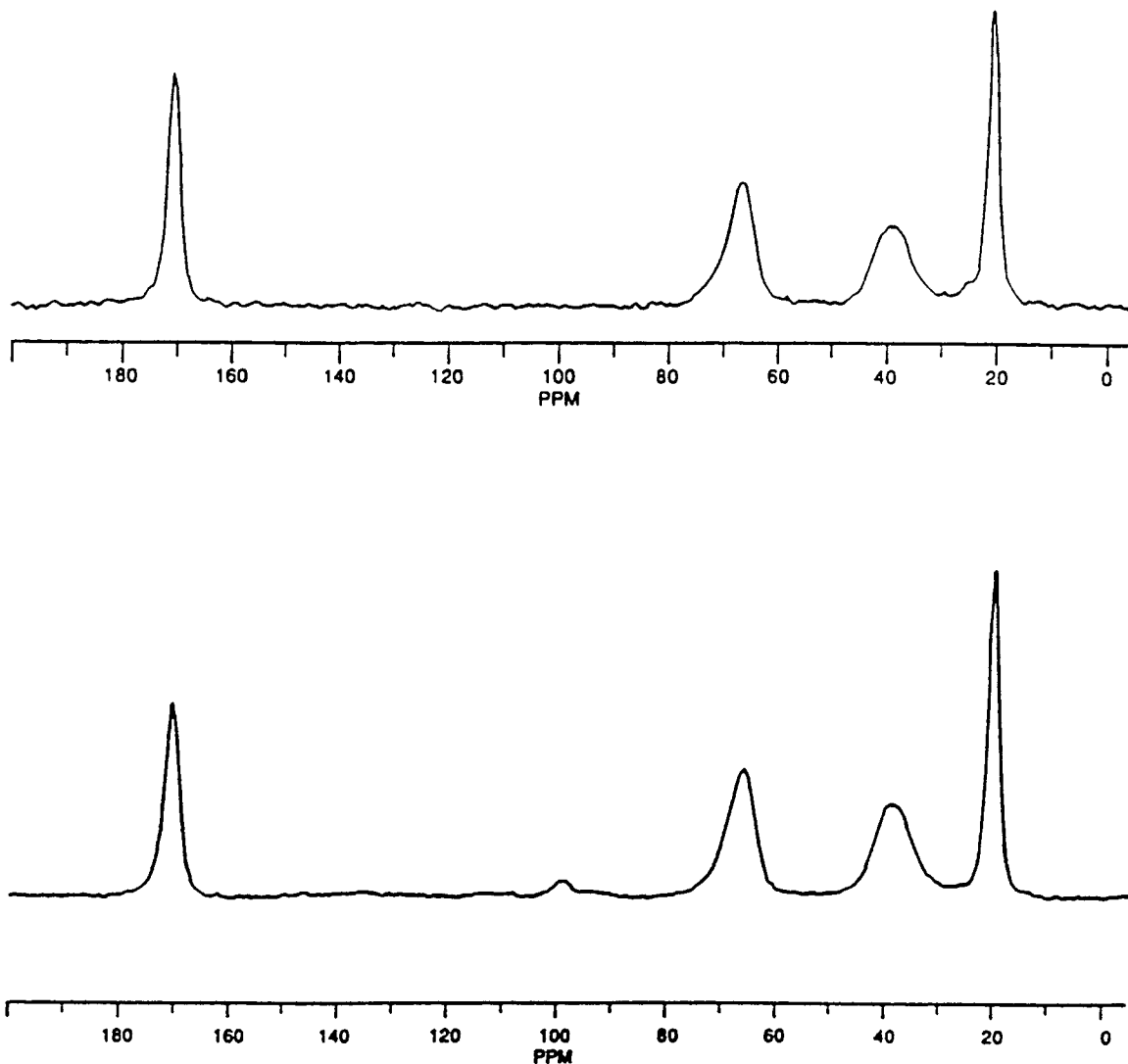
Figure 5 ^{13}C CP/MAS NMR of: (a) PVAc (top); (b) PVAc after UV/SO$_2$ 96 h exposure (bottom).

sulfoxide, sulfone, sulfinic acid, or sulfate groups occur. The sulfur incorporation data also demonstrate that butyl acrylate has a strong co-unit effect. The data for the VC/VAc copolymer conversely suggest vinyl chloride does not exhibit a co-unit effect.

At this point, a physical model of the influence of BA units on copolymer degradation is helpful. The glass transition temperature T_g is a characteristic of the amorphous phase. Changes in T_g provide a measure of structural changes which have occurred. T_g increases significantly for the UV/SO$_2$ or UV/SO$_2$/H$_2$O-exposed BA/VAc/VC copolymer.[1] Roughly speaking, T_g is the temperature at which the polymer chain segments have acquired sufficient thermal energy for large-scale rotational

motion or considerable torsional oscillation to occur. Below T_g, these motions are very infrequent and the majority of the chain segments have relatively fixed conformations. The presence of BA units in a copolymer can lower T_g. Prior to exposure, T_g is approximately 7°C for VC/BA, 5°C for VAc/BA, 23°C for BA/VAc/VC, and 37°C for MMA/BA reported in this paper.[1,3] The T_g is lowered progressively as the BA content of the copolymer increases. If the BA content is sufficiently large, T_g can be well below 40°C, the temperature at which the exposures were conducted. Thus the available number of conformation changes are increased allowing a greater number of photochemical reactions to occur.

As photodegradation progresses, T_g increases,[1]
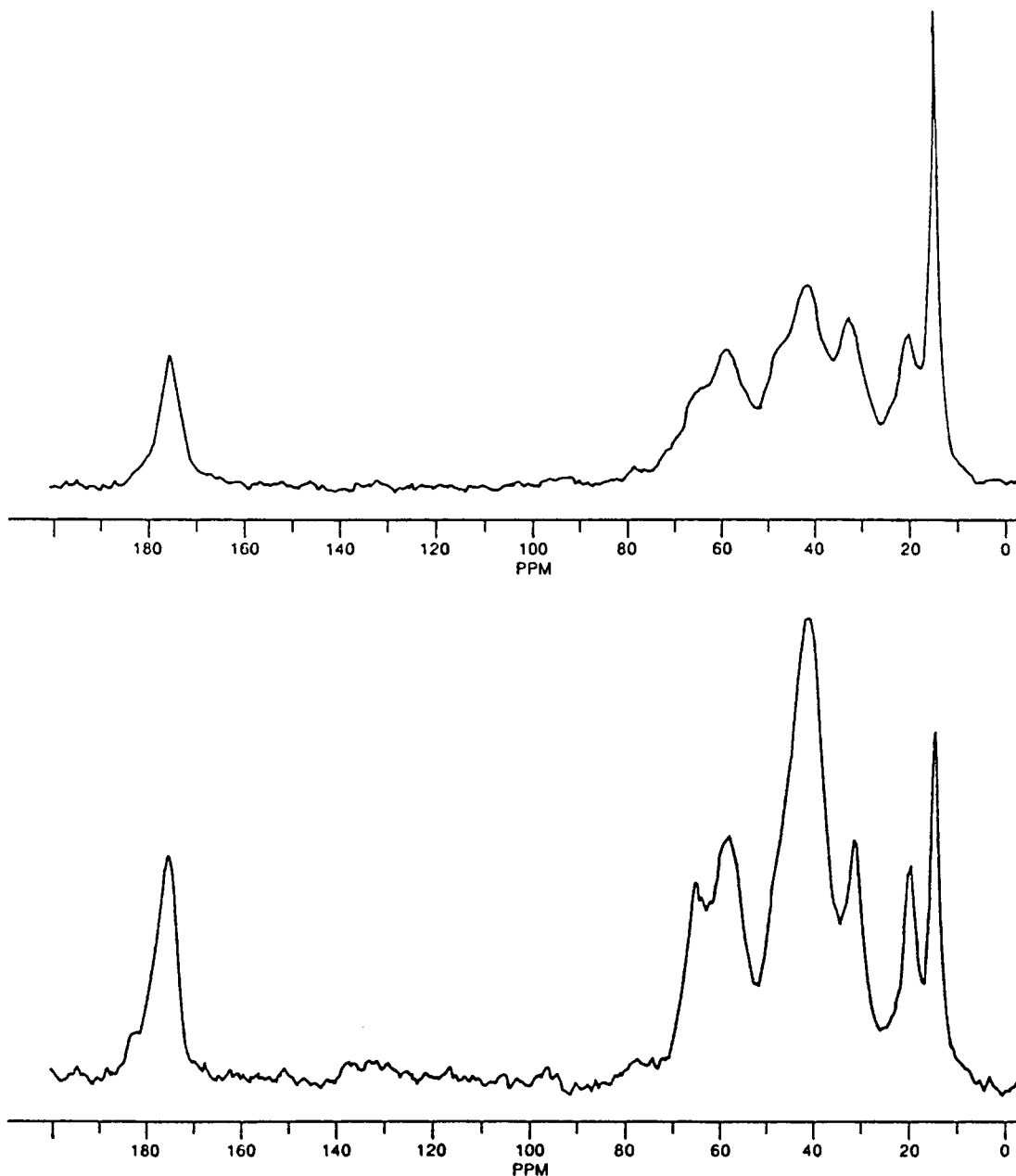
Figure 6 ^{13}C CP/MAS NMR of: (a) VC/BA copolymer (top); (b) VC/BA copolymer after UV/SO$_2$/H$_2$O 96 h exposure (bottom).

sulfur and oxygen contents increase, the available number of conformations decreases (available number of possible sites for sulfate or sulfone attachment decreases), and eventually the sulfur and oxygen contents will not increase. However, over the time period of exposures in this study, polyene formation continues to further darken the film as the exposure continues. Eventually, the copolymer film becomes more brittle, decomposes, and breaks

apart. Since the T_g of unexposed PBA is approximately $-60°C$, it has high permeability to oxygen molecules at room temperature.[11] The resultant photochemistry of PBA or BA copolymers is therefore sensitive to the ambient oxygen concentration surrounding the film. Similarly, the BA/VAc/VC copolymer absorbs large amounts of SO$_2$.[8] Presumably SO$_2$ permeates the copolymer films, participates in photochemical reactions with the copolymer, and
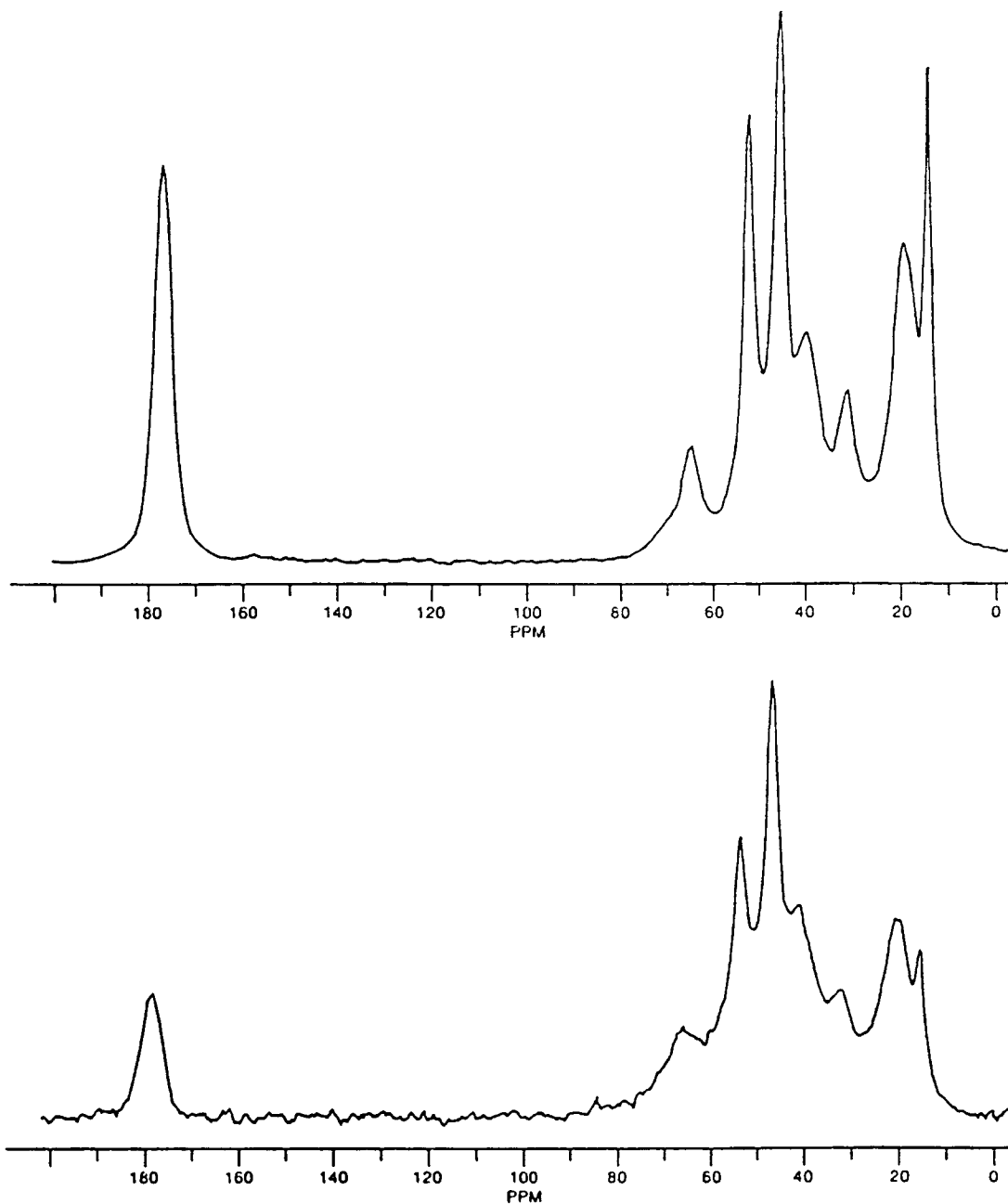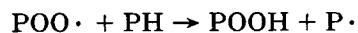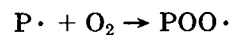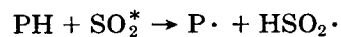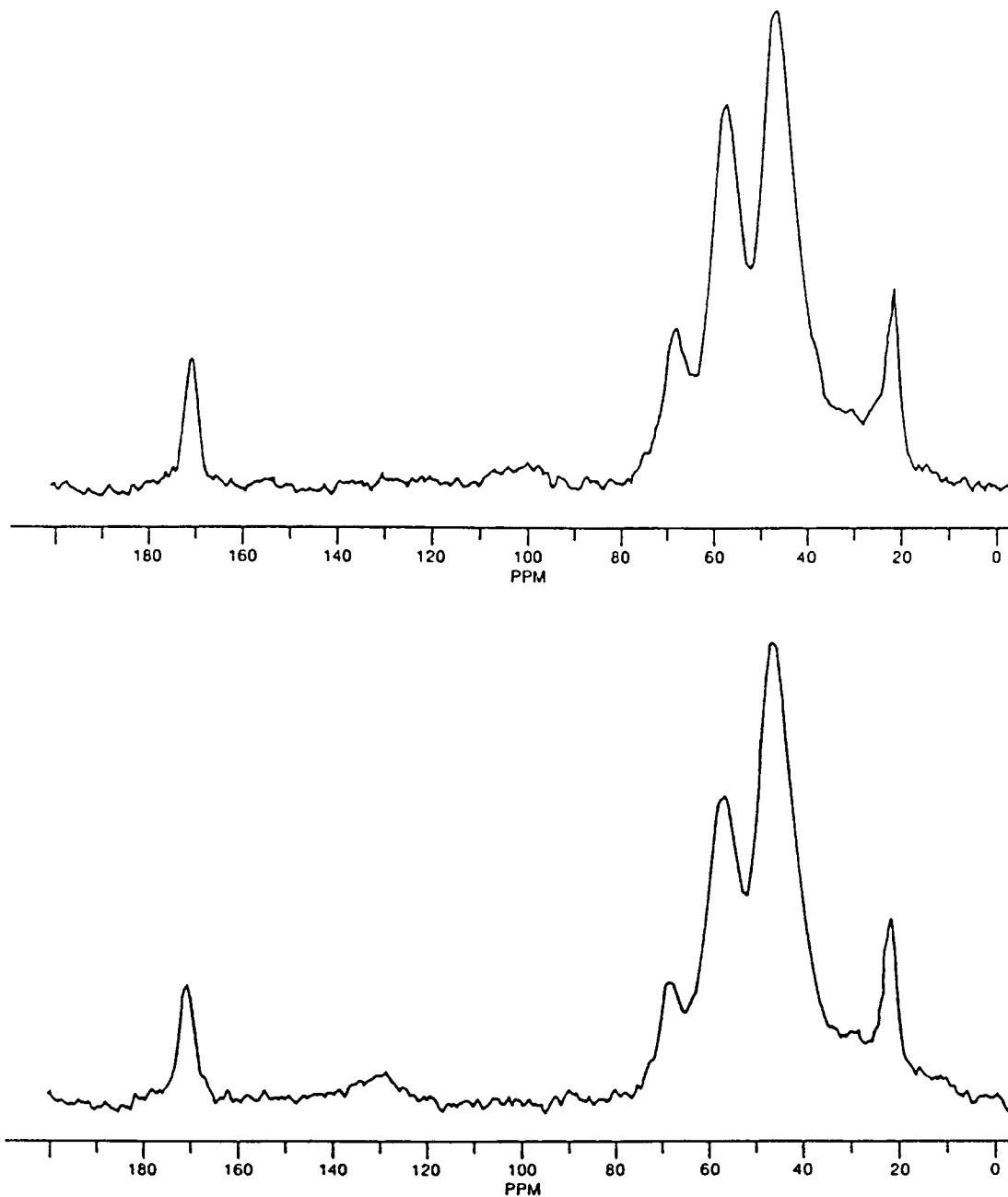
Figure 7 ^{13}C CP/MAS NMR of: (a) MMA/BA copolymer (top); (b) MMA/BA copolymer after UV/SO$_2$/H$_2$O 96 h exposure (bottom).

becomes bonded to the copolymer to produce the observed S concentration increase for the UV/SO$_2$ (Tables II and III) or UV/SO$_2$/H$_2$O-exposed BA-type copolymer.
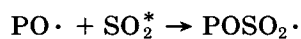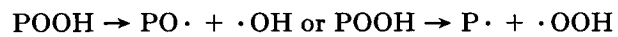
Reaction of the polymer structural units (PH) with photoactivated SO$_2$ (SO$_2^*$) initiates photodegradation, including hydroperoxide group formation (oxygen is assumed to be present), which ultimately produces pendant sulfate groups and other degradation products[1-3]:
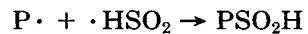
$$PH + SO_2^* \rightarrow P\cdot + HSO_2\cdot$$

$$P\cdot + O_2 \rightarrow POO\cdot$$

$$POO\cdot + PH \rightarrow POOH + P\cdot$$

Figure 8 ^{13}C CP/MAS NMR of: (a) VC/VAc copolymer (top); (b) VC/VAc copolymer after UV/SO$_2$/H$_2$O 96 h exposure (bottom).

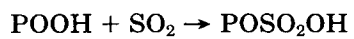$$POOH \rightarrow PO\cdot + \cdot OH \text{ or } POOH \rightarrow P\cdot + \cdot OOH$$

$$PO\cdot + SO_2^* \rightarrow POSO_2\cdot$$

$$POSO_2\cdot + \cdot OH \rightarrow POSO_2OH$$

(sulfate pendant group)

$$POOH + SO_2 \rightarrow POSO_2OH$$

(sulfate pendant group)

$$P\cdot + \cdot OH \rightarrow POH$$

(hydroxyl pendant group)

$$P\cdot + \cdot HSO_2 \rightarrow PSO_2H$$

(sulfone pendant group) or

$$P\cdot + SO_2 \rightarrow \cdot PSO_2 \text{ and}$$

$$\cdot PSO_2 + PH \rightarrow P\cdot + PSO_2H$$

$$P\cdot \rightarrow -CH{=}CH- \; + \; R\cdot$$

(polyene formation, darkening color)

$$(R = -Cl \text{ or } -OCOCH_3)$$
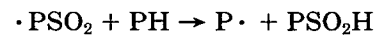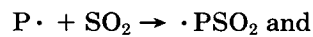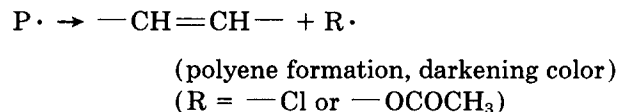
CONCLUSION

^{13}C CP/MAS NMR spectra show clear evidence that several microstructural changes occur in acrylate-type polymers that are exposed to UV/SO$_2$ or UV/SO$_2$/H$_2$O. Exposure of the films in the presence of UV/SO$_2$ or UV/SO$_2$/H$_2$O results in the incorporation of pendant sulfate, sulfone, and sulfinic acid groups which are associated with chemical shifts that appear in the ^{13}C NMR spectra near 76 ppm and in the 30–60 ppm range. For UV/SO$_2$- or UV/SO$_2$/H$_2$O-exposed copolymer films, it has been suggested that the observed changes in the NMR spectra and elemental concentrations may be associated with a co-unit interaction between BA and VAc units in the copolymer. The co-unit interaction appears to increase the rate of formation of a peak at ca. 76 ppm associated with incorporation of pendant sulfate groups. Evidence presented here shows that the combination of solid-state NMR and elemental analysis may be used to investigate the contribution of co-unit interactions to copolymer photodegradation. More importantly, the results of this investigation are significant in view of the increasing interest in environmental degradation of polymers and the effects of acid rain on polymeric coating materials.

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