

Characterization of Flame Retarded Polymer Combustion Chars by
Solid-State ^{13}C and ^{29}Si NMR and EPR

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INTRODUCTION: Additives that increase the amount of charcoal-like residue or carbonaceous char that forms during polymer combustion are very effective fire retardants¹. However, very little is understood about the detailed structure of char or how it forms. Our research efforts focus on reducing polymer flammability by promoting char formation. Char formation reduces the amount of small, volatile polymer pyrolysis fragments, or fuel, available for burning in the gas phase; this in turn reduces the amount of heat released and fed back to the polymer surface. The char also insulates the underlying polymer, due to its low thermal conductivity, and reradiates externally impinging energy away from the polymer. The char must also function as a mass transport barrier, by physically delaying the volatilization of decomposition products and or trapping decomposition products through chemical reaction. The physical structure of the char is important in this role. Thick, foamy char appears to be more fire resistant than brittle, thin char. This char enhancing approach is most successful when the polymer chars rapidly and early in the burning process². To be useful, the charring process must occur at a temperature above the polymer processing temperature but below the temperature where rapid gasification of the polymer to combustible fuel occurs.

BACKGROUND: Elsewhere, we have reported that silica gel³ combined with potassium carbonate is an effective fire retardant for a wide variety of common polymers such as polypropylene (PP), nylon-6,6, polymethylmethacrylate (PMMA), poly (vinyl alcohol) (PVA), cellulose, and to a lesser extent polystyrene (PS) and styrene-acrylonitrile (SAN)⁴. Typically, these additives reduce the peak heat release rate by two thirds, without significantly increasing the smoke or carbon monoxide levels during polymer combustion. We found that, for polymers like PP, nylon, PMMA and PS, the silica gel /K₂CO₃ additives do not significantly affect the heat of combustion. It was proposed that for PP, nylon, PMMA and PS, these additives act primarily in the condensed phase, not in the gas phase. For PVA and cellulose the results indicated a combination of mechanisms of action. In addition to the enhanced charring effect and the resulting reduction in mass loss rate, the heat of combustion and the smoke were reduced. It was proposed that the additives may increase the rate of H₂O elimination from cellulose and PVA. This dilution of the combustible gases may be responsible for the reduction of the specific heat of combustion, and for the reduction of the smoke. In this preprint, we report on our efforts to determine mechanistically how these additives reduce polymer flammability.

CHAR CHARACTERIZATION: ^{29}Si NMR: One possible mechanism of action for these additives is through the formation of a potassium silicate glass during the combustion. In earlier work on fire retardants, silicates were claimed to be quite effective⁵. We characterized the char from the combustion in the Cone calorimeter of poly(vinyl alcohol) (PVA) with silica gel /K₂CO₃ additives (mass ratio, 90:6:4 respectively) using single pulse magic angle spinning (SP/MAS) ^{29}Si NMR. The SP/MAS ^{29}Si spectrum (not shown) shows a broad resonance from -130 ppm to -90 ppm, which indicates that the residue may contain some silicate species. Comparison of this spectra to the SP/MAS ^{29}Si NMR spectra of the char from combustion of PVA with sodium silicate (mass ratio 90:10) (not shown) confirms this possibility, since both spectra show the majority of the silicons are of the Q³ [(SiO)₃SiO(-)] (100 ppm to 110 ppm) and Q⁴ [(SiO)₄Si] (110 ppm to 120 ppm) type. However, SP/MAS ^{29}Si NMR can not distinguish between silicate (SiO(-)) and silanol (SiOH) silicons. Cross-polarization (CP)/MAS ^{29}Si NMR, which selectively enhances the signal intensities of Si nuclei near protons, can accomplish this, but only in a qualitative manner. The CP/MAS ^{29}Si spectrum (not shown) of the PVA with silica gel /K₂CO₃ char reveals that there is still a significant fraction of Q² [-(SiO)₂-Si-(OH)₂] (85 ppm to 95 ppm) and Q³ [-(SiO)₃-Si-OH] (95 ppm to 105 ppm) silanol functionality present after the combustion. Silanol is also present in the original silica gel structure. SP/MAS and CP/MAS ^{29}Si spectra, similar to those discussed above, are reported in the literature for silica gels⁶. This MAS ^{29}Si NMR data indicates that the majority of the silica gel original structure remains intact during the combustion. However, these spectra do not allow a quantitative analysis. This data does raise the possibility that silica gel itself is directly affecting the flammability, either chemically in a catalytic process or physically.

MAS ^{13}C NMR: We have attempted to determine the effect of the individual additives on the carbonaceous structure of the char by characterizing the char using MAS ^{13}C NMR techniques. Other research groups, as well as our own, have used these techniques to study polymer degradation processes^{7,8,9,10,11}. Previously, we found that these techniques, when used to characterize the intermediate decomposition products of pure PVA (formed at 250°C to 400°C, 30 min in N_2), were very useful in exploring the various pathways involved in the PVA pyrolysis¹². However, several problems potentially interfere with making quantitative measurements of the intensities of ^{13}C NMR signals in experiments carried out on combustion chars, and with drawing conclusions using these data. First, since these combustion chars are hydrogen-depleted carbon-rich materials, there may be a significant fraction of carbons which, are more than ~ 0.5 nm from protons and, therefore, will not readily cross polarize, and will not be properly represented in the CP/MAS ^{13}C signal¹³. Secondly, these chars may contain significant concentrations of paramagnetic centers (e.g., particles with unpaired electrons, free radicals). Paramagnetic centers can potentially broaden or shift resonances of ^{13}C carbons in the local (0.5 nm - 1.5 nm) environment around the radicals, preventing these carbons from being observed in either CP/MAS or SP/MAS ^{13}C NMR experiments. The range and nature of the influence of an unpaired electron on the ^{13}C signals depends on the spin lifetime (T_1^e) of the electron. When $T_1^e \leq 10^{-8}$ s, fewer spins are perturbed directly and it is mainly the ^1H spin-lattice relaxation time (T_1^{H}) and the ^{13}C spin-lattice relaxation time (T_1^{C}) which are shortened. On the other hand, when $T_1^e \geq 10^{-6}$ s, many more nuclear spins are strongly perturbed and the rotating frame relaxation time ($T_{1\rho}$) is shortened much more than T_1^{H} . With short $T_{1\rho}$'s, the CP intensities will be weaker and more distorted with respect to protonated and non-protonated carbons. Aside from the influence of unpaired electrons, a proton-depleted solid can also possess carbons with very long T_1^{C} 's. Thus, single pulse MAS ^{13}C NMR experiments may also under represent the carbons, in combustion char samples, if scans are repeated too frequently¹⁴. For these reasons CP/MAS and SP/MAS ^{13}C spectra may only be representative of a fraction of the carbons present in combustion chars. Bourbigot et. al. have observed these type of effects in CP/MAS ^{13}C NMR studies of a commercial polymer flame retardant system. In the CP/MAS ^{13}C spectrum of the polymer flame retardant additive char, prepared at 430°C, a disappearance of the aromatic band was attributed to the presence of free radicals "trapped" in the material. Indeed, subsequent electron paramagnetic resonance (EPR) analysis showed a radical concentration of $\sim 10^{19}$ spins/g⁶. Muntean et. al. have done a quantitative study of these effects on CP/MAS and SP/MAS ^{13}C measurements in coals. Single pulse (90°)/MAS ^{13}C spectra of coal samples containing high concentrations of paramagnetic centers ($\sim 10^{19}$ spins/g) were found to have greater percent carbon observed in the sample ($\%C_{\text{obs}}$, 43 % to 70 %) than CP/MAS ^{13}C spectra, which showed $\%C_{\text{obs}}$ from 26 % to 55 %¹⁵.

In view of the above, we choose to use SP(90°)/MAS ^{13}C NMR to attempt to obtain as quantitative a characterization of the chars as possible. Analysis of these PVA combustion chars, by EPR, revealed moderate to high concentrations (10^{18} to 10^{19} spins/g) of paramagnetic centers. A calculation based on the EPR data, which assumes that each radical obscures all ^{13}C nuclei within a spherical volume with a radius of 1 nm, reveals, if the radicals are assumed to be distributed uniformly in the char, that only about 1 % to 10 % of the carbons should be obscured at these radical concentrations (10^{18} to 10^{19} spins/g). A similar analysis by Muntean et. al. is in agreement with this calculation¹⁶. The SP/MAS ^{13}C spectra of the chars of: PVA with silica gel and K_2CO_3 (mass ratio: 90:6:4), PVA with silica gel only (mass ratio: 90:10), and of pure PVA, are shown in Figure 1. To attempt to determine $\%C_{\text{obs}}$ in these SP/MAS spectra, by spin counting measurements, and to determine the carbon-to-hydrogen ratio, elemental analysis was done on each char sample. However, severe inconsistencies between this data, x-ray photoelectron spectroscopy (XPS) data and calculations based on the char yields, make it impossible at this time to determine the fraction of ^{13}C nuclei observed in the samples. For the char of PVA with silica gel / K_2CO_3 a variable pulse width series of experiments were done; these confirmed that no intensity was lost due to saturation. The major feature of the SP/MAS spectra for these chars is a broad resonance in the aromatic-olefinic region from 110 ppm to 150 ppm. The absence of any strong signal in the aliphatic region indicates that these materials consist mostly of aromatic-olefinic type carbon, although poor signal-to-noise, in the spectra of the chars with additives, prevents making a quantitative conclusion about the exact aromatic to aliphatic carbon ratio.

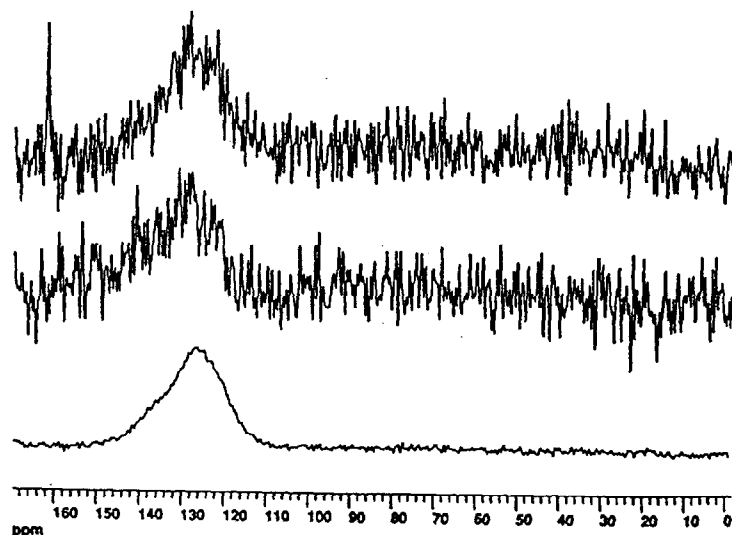


Figure 1. The SP/MAS ^{13}C spectra of the chars of: PVA with silica gel and K_2CO_3 (mass ratio: 90:6:4) (top), PVA with silica gel only (mass ratio: 90:10) (middle), and of pure PVA (bottom). The major feature of these SP/MAS spectra is the broad resonance in the aromatic-olefinic region from 110 ppm to 150 ppm.

One of the goals of this work is to determine the role non-protonated carbon, present in the char, plays in controlling char performance, and flammability. Since these type of carbons should be part of crosslinks and or graphitic type structures, their presence may improve the performance of the char by increasing thermal stability and improving mechanical strength. A particularly useful ^{13}C NMR experiment for characterizing chars, which allows observation of the non-protonated carbons in the char is the interrupted

decoupling (ID) experiment¹⁷. However, due to signal-to-noise limitations we have not been able to obtain suitable ID SP/MAS ^{13}C spectra. Since the CP/MAS spectra should give a good representation of protonated carbons in the char, by virtue of their ease of cross polarization, we felt the ID CP/MAS ^{13}C data would provide the best characteristic lineshape of the protonated carbon of the chars. This approach gives a suitable method for partitioning the SP/MAS signal into its' non-protonated carbon (C_{NP}) and protonated carbon (C_{P}) components.

An example of our method of obtaining the C_{P} lineshape for the char of PVA with silica gel (mass ratio: 90:10) using CP/MAS ^{13}C NMR and ID-CP/MAS ^{13}C NMR techniques is described below. The CP/MAS ^{13}C and ID-CP/MAS ^{13}C spectra of the char of PVA with silica gel is shown in Figures 2. The normal CP/MAS ^{13}C NMR, shown in the middle of the figure, contains a broad resonance in the aromatic-olefinic region from 110 ppm to 150 ppm and two weaker broad signals in the aliphatic region, one centered at 20 ppm and the other at 35 ppm. This spectrum shows that, ~10 % of the carbons that cross polarize are aliphatic (sp^3) carbons in this char. The ID-CP/MAS spectrum, the bottom spectrum in Figure 2, reveals only the non-protonated carbons which have cross-polarized. Comparison of the ID-CP/MAS spectra (bottom) to the normal CP/MAS spectra (middle) shows that the downfield shoulder in the CP/MAS spectra, at 135 ppm, is due to non-protonated aromatic-olefinic carbons. The result of subtracting the appropriate intensity of the ID-CP/MAS spectrum from the CP/MAS spectrum, so that the downfield shoulder is removed, is shown in the top of the figure. This is our best estimate of the lineshape for the protonated carbons in the PVA with silica gel char.

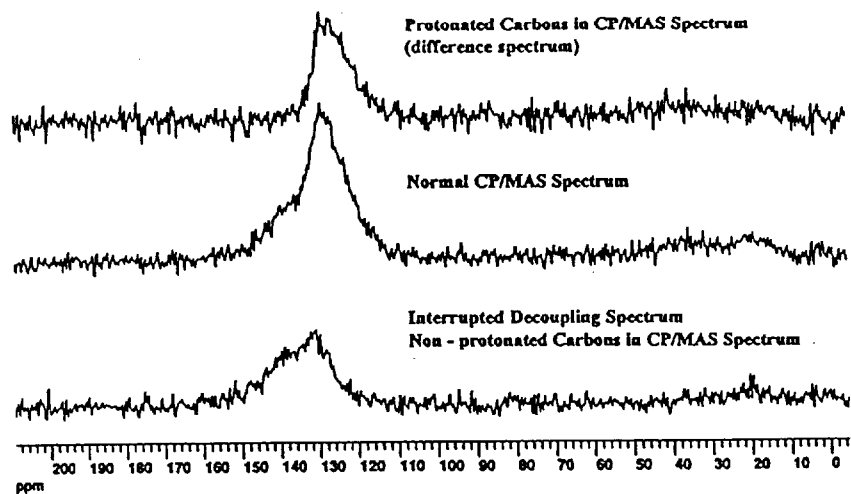


Figure 2. The CP/MAS ^{13}C spectra of the char of PVA with silica gel. The normal CP/MAS ^{13}C spectrum is shown in the middle. The ID-CP/MAS spectrum (bottom) reveals only the non-protonated carbons which have cross-polarized. The difference spectrum (top), obtained by subtracting the appropriate intensity of the ID-CP/MAS spectrum from the CP/MAS spectrum, gives the spectrum of the protonated carbons that cross-polarized.

Figure 3 shows the result of subtracting the appropriate intensity of the protonated carbon (difference) spectrum (bottom) from the SP/MAS spectrum (middle), so that the upfield portion of the line is removed, yielding the non-protonated carbon (difference) spectrum (top). The rationale for complete removal of the upfield portion of the aromatic-olefinic resonance is based on the belief that this region of the spectrum is usually dominated by protonated aromatic-olefinic carbons.

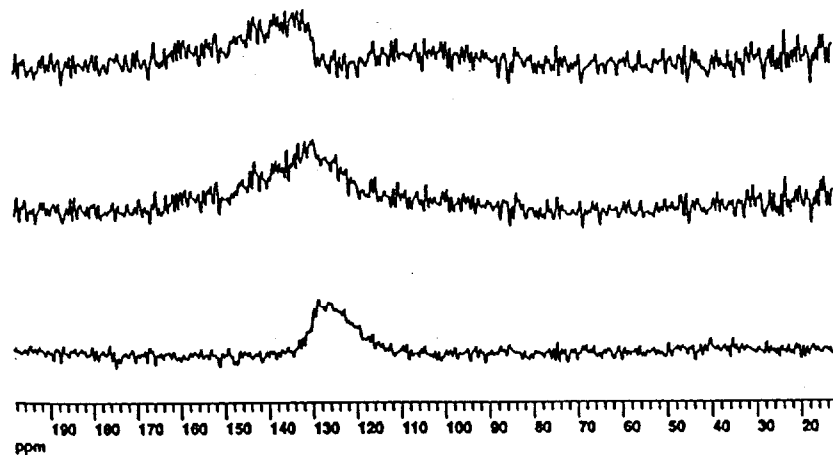


Figure 3. The non-protonated carbon SP/MAS ^{13}C spectrum of the char of PVA with silica gel (top), generated by subtracting the appropriate intensity of the protonated carbon spectrum (bottom) from the SP/MAS ^{13}C spectrum (middle), so that the upfield portion of the line is removed.

Comparison of the intensity of the non-protonated to protonated aromatic-olefinic carbon spectra gives a C_{NP} to C_P ratio of ~ 1.5 to 1.0 ¹⁸ for this sample.

Using this same method for the other two chars (PVA with silica gel and K_2CO_3 (mass ratio: 90:6:4), and pure PVA) i.e., subtracting the protonated carbon (difference) spectra, obtained from the respective CP/MAS spectra, from the SP/MAS spectra for these chars, we are able to make the best estimate of the ratio of C_{NP} to C_P . This ratio is also ~ 1.5 to 1.0 for these chars. That is, all three chars have the same C_{NP} to C_P ratio (1.5 to 1.0).

CONCLUSIONS: To the extent that this approach to characterizing these materials accurately reflects the sample-wide chemistries, this data indicates that, even though the char yields are very different for these three systems (carbonaceous char yield: 5% for pure PVA; 29% for PVA with silica gel; and 43% for PVA with silica gel and K_2CO_3) the carbon structure of the chars are quite similar. It appears that the additives do not change the type of char formed, but they do change the rate of char formation relative to the rate of fuel generation, since the char yield is higher and the flammability (due to a lower fuel generation rate) is reduced. It should be noted that, when only the CP/MAS ^{13}C data were used to characterize these chars different results and conclusions were found, especially for the pure PVA char and the PVA with silica gel char³. The C_{NP} to C_P ratio, from the CP/MAS data, for these chars are: $1.0 : 1.2$ for the pure PVA char, $1.0 : 1.2$ for the PVA with silica gel char, and $1.5 : 1.0$ for the char from PVA with silica gel and K_2CO_3 ¹⁸.

These substantially different results, for the ratio of C_{NP} to C_P , illustrate, for some systems, that there can be uncertainties associated with attempting to quantitatively characterize hydrogen depleted materials that contain paramagnetic centers, using only CP/MAS ^{13}C NMR. Such results may also point to more clustering of protonated carbons in the pure PVA, and the PVA with silica gel chars. We are continuing to investigate issues of inhomogeneous proton distributions.

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3. Certain commercial equipment, instruments, materials, services or companies are identified in this paper in order to specify adequately the experimental procedure. This in no way implies endorsement or recommendation by NIST.
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