work at the National Bureau of Standards.

Registry No. EB (copolymer), 25087-34-7.

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Investigation of the Thermal Degradation of Poly(acrylic acid) and Poly(methacrylic acid) by High-Resolution ^{13}C CP/MAS NMR Spectroscopy

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ABSTRACT: The structural changes occurring in poly(acrylic acid) and poly(methacrylic acid) when exposed to high temperatures have been investigated by high-resolution ^{13}C solid-state NMR. The initial step in the decomposition of poly(acrylic acid) involves the formation of anhydrides, the majority of which involve six-membered rings. Continued heating results in the loss of hydrogen from the backbone of the polymer. At higher temperatures, a highly aromatic char with phenol functionalities is formed. Poly(methacrylic acid) also forms six-membered cyclic anhydrides but forms a stable structure at lower temperatures. At much higher temperatures substantial degradation occurs, giving rise to an aromatic char that has phenol functionalities as well as methyl and quaternary carbons.

Introduction

The present work employs high-resolution ^{13}C CP/MAS solid-state NMR spectroscopy to analyze the solid products of the thermal degradation of poly(acrylic acid) and poly(methacrylic acid). In these experiments, a combination of cross-polarization[1] (CP) and "magic-angle" spinning[2] (MAS) with high-power proton decoupling is used to give ^{13}C NMR spectra of moderate to good resolution from completely solid materials.[3,4] The spectra yield the isotropic average chemical shifts (for the solid state) and can be used for structural elucidation by employing the chemical shift correlations from solution ^{13}C NMR as reference data. These techniques have found wide application in the study of insoluble and amorphous materials,[5] where information is severely limited by the lack of a good analytical technique, diffraction techniques not being applicable because of the lack of long-range order. It is also possible to determine additional information

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regarding the contributions to the total spectrum from both the nonprotonated and protonated carbons by using a modification of the CP/MAS pulse sequence developed by Opella.[6]

The solid products formed during the thermal degradation of polymers are generally insoluble and amorphous, making analysis difficult. Solid-state NMR has been shown to be a suitable technique to follow structural changes occurring during the thermal degradation of these materials.[7] From the knowledge of the structure of the solid products formed during the decomposition, considerable information about the mechanism of these processes can be obtained.

Poly(acrylic acid) and poly(methacrylic acid) are both known to degrade when exposed to high temperatures. The purpose of this study is to follow the changes occurring in these polymers at elevated temperatures by monitoring the chemical functionalities present in the degraded resin as a function of time and temperature. Previous workers have studied these systems[8,9] by using IR spectroscopy to study the solid products and a number of different techniques including mass spectroscopy, chemical analysis, and chromatography to monitor the volatile products of the decomposition.

Experimental Section

^{13}C CP/MAS NMR spectra were recorded at 22.6 MHz on a Bruker CXP-100 spectrometer equipped with a home-built probe with an Andrew–Beams type spinning apparatus. The sample spinners were constructed by KEL-F [poly(chlorotrifluoroethylene)] with a capacity of ~460 μL and were spun at ~3 kHz with air as a driving gas.

Poly(acrylic acid) and poly(methacrylic acid) were commercially available samples (Polysciences Inc.) and were heated in air for the times and at the temperature indicated in the text. After heating, the samples were cooled and ^{13}C solid-state NMR spectra recorded with the CP/MAS technique to obtain the total spectrum. Spectra were also obtained with the nonprotonated carbon selection experiment[6] to determine the contribution to the spectra due to those carbons which had attached hydrogen atoms.

All spectra were obtained with a 1-ms contact time, a 1-s delay between pulse sequences, and a decoupling field of 12 G. These conditions have been shown to give reliable spectra for similar amorphous materials. Nonprotonated spectra were recorded under identical conditions but with the proton-decoupling field gated off for ~50 μs before acquisition. During this period, the magnetizations of all carbons with directly bonded protons decay rapidly due to the strong proton dipolar interaction and are not detected during the subsequent acquisition period. Methyl carbon resonances may still be observed due to their particular relaxation properties but they are greatly reduced in intensity.

Results and Discussion

Poly(acrylic acid). Figure 1 shows the solid-state ^{13}C NMR spectra for various heat-treated poly(acrylic acid) samples. In all cases the spectra on the left are the total CP/MAS spectra and those on the right are the corresponding spectra obtained with the nonprotonated carbon selection experiment. Parts A and B of Figure 1 are the ^{13}C spectra of an undegraded poly(acrylic acid) sample. As indicated in the figure, the resonance of δ 180 is due to the acid functionality. The peak at δ 39 has two components due to the methylene and methine carbons of the backbone of the polymer.

Parts C and D of Figure 1 show the effect of heating at 200 °C in air for 1 h. There is a loss of intensity in the resonance at δ 180 and the appearance of a new peak at δ 171 due to a carbonyl functionality. This change corresponds to the formation of anhydrides from the carboxylic acid groups in the polymer. There are several types of anhydrides that could possibly be formed in this polymer. Comparison of the observed chemical shift value with

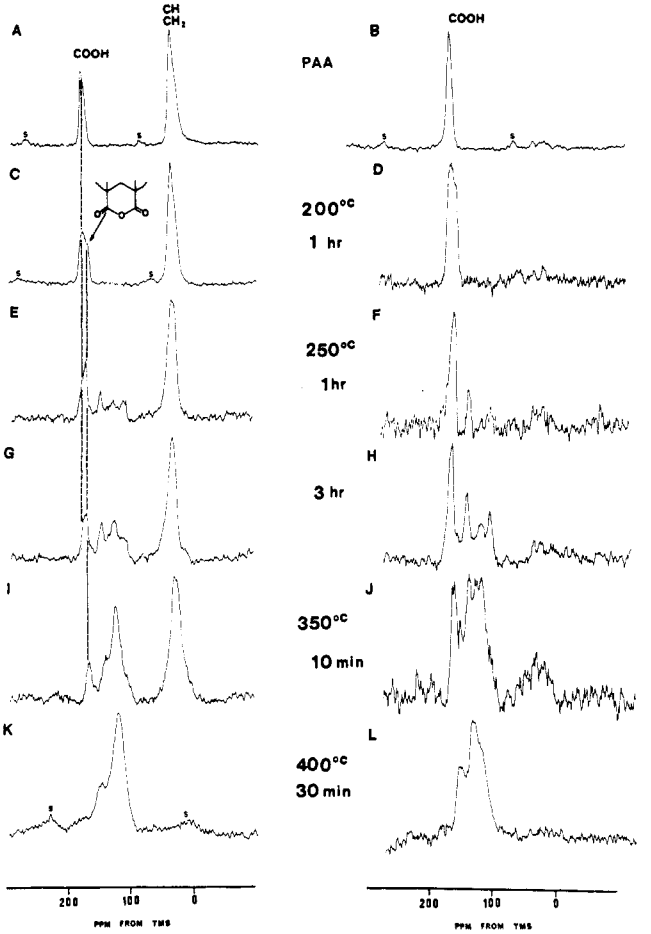
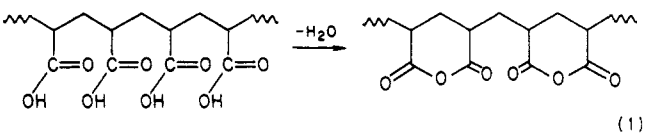


Figure 1. ^{13}C CP/MAS NMR spectra of various poly(acrylic acid) samples. All spectra were obtained with 1-ms contact and 1-s recycle delay. (A) Undegraded poly(acrylic acid) sample; (C) PAA heated at 200 °C for 1 h; (E) PAA heated at 250 °C for 1 h; (G) PAA heated at 250 °C for 3 h; (I) PAA heated at 350 °C for 10 min; (K) PAA heated at 400 °C for 30 min, (B), (D), (F), (H), (J), and (L) are the corresponding spectra obtained with the nonprotonated carbon selection experiment. Small peaks marked "S" denote spinning sidebands.

the ^{13}C chemical shifts of several model compounds[10] in solution (succinic anhydride, representative of five-membered rings (δ 175), 2,4-dimethylglutaric anhydride, representative of six-membered rings (cis δ 171.5, trans δ 171.2), and isobutaric anhydride, typical of open structures (δ 173)) suggests that the resonance can be assigned to carbonyl groups from the formation of six-membered rings as shown in eq 1. Although the chemical shift is also



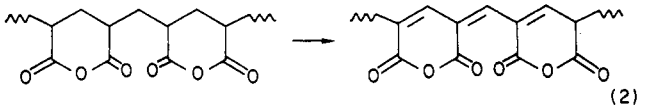
(1)

compatible with the formation of five-membered rings, these would have to come from head-to-head repeat units and are ruled out from the known structure of the polymer.[1]

Continued heating at 200 °C (not shown in the figure) results in further loss of acid functionalities and an increase in the intensity of the anhydride resonance.

If the sample is heated at 250 °C for 1 h, a number of new resonances appear (Figure 1, parts E and F). The peak due to the original acid functionalities has almost completely disappeared and the anhydride resonance now appears to have an unresolved shoulder at δ 173. This is the region where carbonyl groups in anhydrides formed

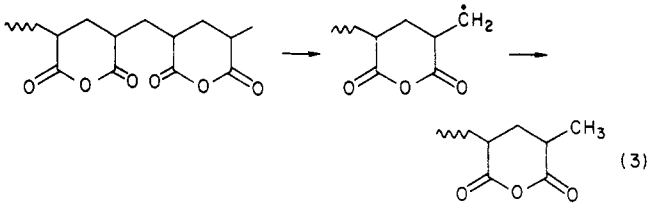
by the reaction of acid groups *between* chains would be expected to resonate (isobutaric anhydride δ 173). There is also a series of peaks in the aromatic region of the spectrum. These peaks arise from the loss of hydrogen atoms from the backbone of the polymer as shown in eq 2. After 3 h the spectra (parts G and H of Figure 1) show



(2)

an increase in the intensity of the resonances in the aromatic region. There also appears to be a slight reduction in the intensity of the anhydride resonance.

Continued heating of the sample at higher temperatures results in massive degradation of the polymer. Parts I and J of Figure 1 show the effect of heating at 350 °C for 10 min. At this stage the sample is becoming increasingly aromatic in nature. There is a continued reduction in the carbonyl intensity, but there is still a large aliphatic resonance which appears to have a shoulder at δ 20 which remains in the nonprotonated spectrum. This is an indication of the formation of methyl functionalities in the matrix, possibly by the breaking of methylenes as shown in eq 3.



(3)

Parts K and L of Figure 1 show the effect of heating the sample at 400 °C for 30 min. The sample has now undergone a large number of structural changes. The aliphatic resonances have almost completely disappeared and there is a new resonance at δ 155. This is in the region where hydroxyl-bearing aromatic carbons would be expected to resonate. There is also the appearance of some weak resonances in the 170–195 region that indicate that oxidation of the sample is occurring.

Thus the ^{13}C solid-state NMR spectra of the various poly(acrylic acid) samples indicate that the initial step in the thermal degradation involves the formation of anhydrides. The majority of these anhydrides involve the formation of six-membered rings by the reaction of adjacent acid groups. As the degradation continues, there appears to be a loss of hydrogen from the backbone of the polymer and also a gradual loss of the carbonyl resonance. At higher temperatures, there is formation of a highly aromatic char that possesses a substantial number of phenol rings. The formation of anhydrides in poly(acrylic acid) has been previously demonstrated by McGaugh and Kottle[8a] using IR spectroscopy. The NMR spectra indicate that anhydride formation is much more extensive than indicated by the IR results. In addition, there is no evidence for the formation of ketones from the NMR spectra, indicating that they are not a *major* product of the degradation.

Poly(methacrylic acid). Figure 2 shows the spectra for various heat-treated poly(methacrylic acid) samples. Parts A and B of Figure 2 are the spectra of an undegraded sample. As indicated in the figure, the resonance at δ 181 can be assigned to the acid functionality of the polymer, the peak at δ 50 to the methylene carbons, and the peak at δ 44 to the quaternary carbon. The resonance at δ 11 is due to the methyl carbons. Parts C and D of Figure 2 show the effect of heating at 250 °C for 1 h. The carbonyl

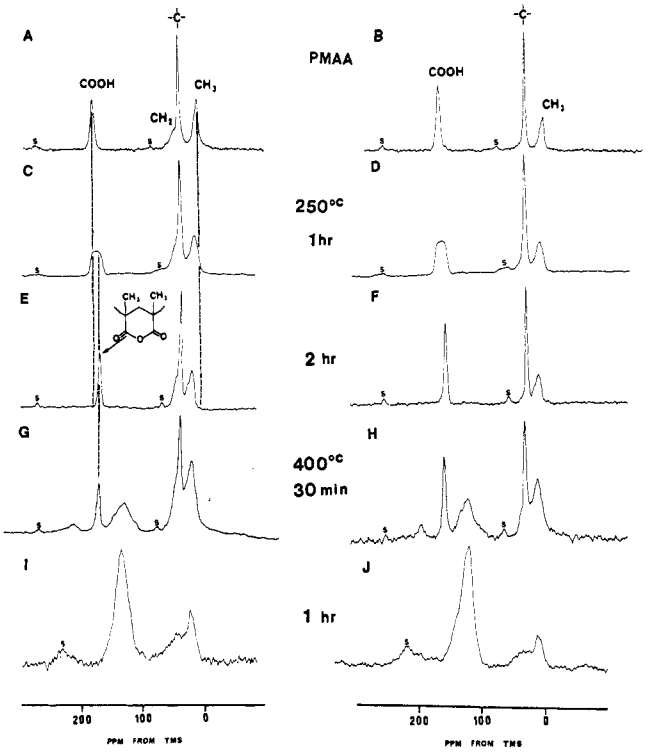
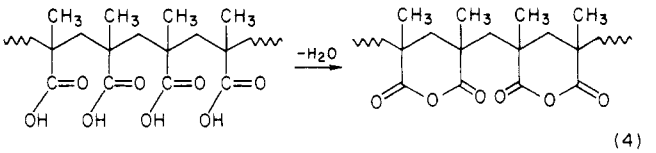


Figure 2. ^{13}C CP/MAS NMR spectra of various poly(methacrylic acid) samples. All samples were recorded with 1-ms contact and 1-s recycle delay. (A) Undegraded poly(methacrylic acid) sample; (C) PMAA heated at 250 °C for 1 h; (E) PMAA heated at 250 °C for 2 h, 5800 scans; (G) PMAA heated at 400 °C for 30 min; (I) PMAA heated at 400 °C for 1 h, 4400 scans. (B), (D), (F), (H), and (J) are the corresponding spectra obtained with the nonprotonated carbon selection experiment. Small peaks marked "S" denote spinning sidebands.

resonance now has two components. The new peak at δ 174 is due to formation of cyclic anhydrides, similar to the case of poly(acrylic acid) as shown in eq 4. This cyclization also gives rise to a shift in the methyl resonance which now appears at δ 16.

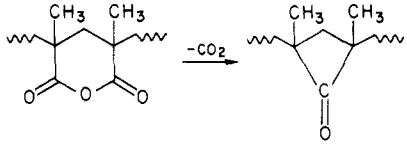


(4)

Heating the sample at 250 °C for 2 h (Figure 2, parts E and F) results in the complete loss of the peak due to the acid functionalities. The peak at δ 174 is now due to anhydride groups. This resonance is reasonably narrow, indicating a high preference for cyclization over the formation of anhydrides between polymer chains and the formation of a surprisingly regular polymer in which all of the acid functionalities have formed cyclic anhydrides and there are no isolated unreacted acid groups. The methyl resonance now appears at δ 20 due to the cyclization of adjacent acid functionalities.

At this stage a stable polymer appears to have been formed. Heating this sample at temperatures up to 300 °C (not shown in the figure) results in no further change in the NMR spectrum. This is in contrast to the poly(acrylic acid) samples, which begin to form unsaturated functionalities before anhydride formation is complete. The presence of methyl groups along the backbone of the methacrylic acid polymer hinders the formation of unsaturated functionalities and greatly stabilizes the polymer since elimination reactions would now require the breaking of C–C bonds.

At the much higher temperature of 400 °C, the sample undergoes extensive degradation. After 30 min (Figure 2, parts G and H), the spectra show peaks due to the cyclized polymer as well as resonances due to aromatic structures. There is also a peak at δ 205, indicating the presence of ketone functionalities. Ketones could be formed by the decarboxylation of the anhydrides, as shown in eq 5. The



(5)

nonprotonated carbon spectrum also shows an additional resonance at δ 43 that must be due to a quaternary carbon. After 1 h (Figure 2, parts I and J), the sample is mainly aromatic in nature. There is a shoulder at δ 151, possibly indicating the formation of some phenol rings and also a number of absorptions in the aliphatic region. There are resonances in the δ 17–22 region, indicating the presence of methyl groups and a series of resonances in the δ 30–50 range, a small part of which may be due to spinning sidebands from the aromatic resonances. This chemical shift range is where methylene functionalities would be expected to resonate. The nonprotonated carbon selection experiment reveals that part of this resonance is due to quaternary carbons. At this stage, the sample has been extensively degraded and has lost ~75% of its original weight.

The spectra thus indicate that the initial step in the thermal degradation of poly(methacrylic acid) is the formation of anhydrides from pendant acid groups to form a regular and quite stable polymer structure. Application of much higher temperatures results in extensive degradation of the polymer to give a large weight loss and the formation of a highly aromatic product that possesses some phenol rings as well as a large number of methyl functionalities. There are also some methylene and quaternary carbons present that link the aromatic sections together. Similar types of structures have previously been observed in the degradation products of other polymer systems.[7]

The thermal degradation of poly(methacrylic acid) below 200 °C has previously been studied by Grant and Grassie[9a] using IR spectroscopy. The IR results are consistent with the NMR data reported here, the formation of six-membered rings being the predominant process observed.

Conclusions

Application of high-resolution ^{13}C CP/MAS solid-state NMR to the thermal degradation of poly(acrylic acid) and poly(methacrylic acid) yields information about the structures of the solid products formed. In both polymers the initial step in the degradation is the formation of cyclic six-membered anhydride groups from the acid functionalities.

In the case of poly(acrylic acid), degradation continues above with the loss of hydrogen from the backbone of the polymer to form alkene functionalities. At higher temperatures, 350 °C and above, a highly aromatic structure is formed which appears to have a considerable number of phenol type structures.

Poly(methacrylic acid) unlike poly(acrylic acid) appears to form a stable and well-defined cyclic anhydride structure at lower temperatures (below 350 °C). At high temperatures it also undergoes massive degradation to yield a highly aromatic structure with phenolic groups but also methyl functionalities and linking methylene and quaternary carbons.

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