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High-Temperature MAS 1D and 2D NMR for Molecular Structure Characterization of Insoluble Polymers

Khalid A.M. Thakur,* Richard A. Newmark, Nicole T. Kuehn, and Travis Q. Gregar

3M Corporate Analytical Technology Center, 3M Center, 201-BS-08, St. Paul, Minnesota 55144

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ABSTRACT: High-resolution solid-state NMR spectra can be obtained of cross-linked and high molecular weight polymeric materials by using a combination of magic-angle spinning and high temperature. The resolution of the spectra can be comparable to that seen in solution NMR spectroscopy. This enables standard solution 2D NMR pulse sequences, such as COSY, TOCSY, and HMQC, to be used to assign resonances in these systems. It has been found that short duration pulse sequences work better than long sequences. For observing heteronuclear correlations, carbon-detected 2D pulse sequences appear to have less stringent instrumental setup requirements than proton-detected 2D sequences.

Introduction

Chemical shifts of resonances obtained in solution NMR spectra have been routinely used for molecular structure identification and characterization of organic solutes.[1−4] In solution, the organic solutes undergo motion in all degrees of freedom, including rotational and translational movement, that is faster than the time scale of the NMR measurement, viz. microseconds. As a result, the observed resonances are at the isotropic chemical shift and are representative of the molecular structure and electronic environment averaged over all orientations with respect to the B_0 (static magnetic field) direction. The intensities of the various resonances are usually proportional to the relative mole fractions of the respective nuclei in the solution.

During NMR measurements of rigid and semirigid materials, the rotational and translational motions are not rapid enough to average out resonance broadening effects due to the presence of (1) a distribution of orientations with respect to the static magnetic field and (2) a distribution of electronic environments due to disorder and defects. Solid-state NMR spectrometers use magic-angle-spinning (MAS) to mechanically average the former during the data acquisition.[5−7] However, MAS does not significantly alter the effects of the latter.

In rigid systems, the use of ^{13}C cross-polarization from ^{1}H spin magnetization while spinning at the magic angle (CP-MAS) has been quite effective in obtaining NMR spectra.[8,9] Here high-power proton decoupling is used during the NMR data acquisition to isolate the sparsely abundant ^{13}C nuclei from the surrounding abundant ^{1}H nuclei, so that spin−spin coupling effects are reduced. However, if the material is not well ordered or highly crystalline, the CP-MAS spectral resonances are significantly broader than those observed in solution NMR spectra. Disorder in the rigid material under investigation can broaden the NMR resonances to a point where molecular structure identification can be a challenge.

The broadening of NMR spectral resonances by chemical shift anisotropy (CSA) effects is “inhomogeneous” and normally averaged by MAS.[5,6] However, the broadening of the FT NMR spectra caused by spin diffusion and orientation-dependent spin−spin interactions is “homogeneous”. Spin diffusion processes (i.e., spin flip-flops) are a result of spin−spin dipolar couplings and require that the relative orientation of the interacting nuclei spins (with respect to B_0 field direction) not change significantly for certain time duration. High-frequency reorientations, as in MAS speeds greater than 15 kHz or rf decoupling, can be effective in reducing “homogeneous” broadening.[5,6,10−12] The “homogeneous” resonance broadening effects are most pronounced in ^{1}H and ^{19}F NMR due to the high natural abundance of these NMR-active nuclei.

It is well-known that ^{1}H and ^{19}F MAS NMR spectra of gels, elastomers, and soft polymeric materials have narrow resonances.[13−17] In a soft/flexible/viscous/viscoelastic polymer, there are rapid fluctuations in position of all surrounding nuclei. These, in addition to averaging the distribution of bond angles and distances during the NMR acquisition, cause rapid dipole orientation changes with respect to the static magnetic field that lead to a reduction in the efficiency of spin diffusion. The higher the frequency of fluctuations, the lower is the efficiency of spin diffusion and the narrower are the observed ^{1}H and ^{19}F NMR resonances.[10,11] In a soft/viscous polymer, unlike in a dilute solution, the motion is not isotropic due to the presence of chain entanglements and preference for reptation. However, the combination of MAS for isotropic averaging, and high temperature or plasticizing solvent for rapid fluctuations in nuclei positions, can lead to significant narrowing of the NMR resonances.[7,10,11,18,19] Examples include the MAS NMR spectra of cross-linked rubber reported by Zaper and Koenig for cross-linked rubber in 1987 and MAS NMR spectra of amorphous insoluble aromatic polymers reported by Sterna and Smith in 1988.[18,19] Here, the polymer state was converted to a soft viscous or viscoelastic state by application of heat. Since then, the application of this method has been only for polymers that are thermally stable since degradation at high temperatures can be a concern. Munson et al. have shown the progression of ^{19}F NMR spectral line narrowing for fluoropolymers with increasing MAS speeds and increasing temperatures.[10] They reported that the combination of MAS and high temperature provided

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* Corresponding author: e-mail kathakur@mmm.com.

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Table 1. Analysis of Insoluble Polymeric Materials

sample	composition	purpose
I	isotactic poly(propylene) of unknown molecular weight	demonstration of extreme proton MAS NMR line narrowing
II	poly(butyl methacrylate)-*co*-poly(2-ethylhexyl acrylate)-*co*-poly(butane diol dimethacrylate)	representative sample of cross-linked insoluble amorphous polymer
III	poly(caprolactone) initiated by diethylene glycol and terminated by 2-isocyanato ethyl methacrylate	representative sample of partially crystalline polymer and for demonstration of 2D MAS NMR data acquisition

narrower spectral resonances than either MAS or temperature alone.[10]

Here, we report the extreme resonance line narrowing that can be achieved in high-temperature MAS proton NMR of polymers such that resonance splitting from scalar *J*-couplings can be observed. Furthermore, 2D NMR spectra can be acquired using standard solution NMR pulse sequences.

Experimental Section

Solid-state NMR spectra were acquired by spinning the sample in Chemagnetics MAS probes at speeds of 7−9 kHz in a 5 mm rotor or 25 kHz in a 3.2 mm rotor. Data were acquired at temperatures between 22 and 250 °C on a Varian INOVA 400 NMR spectrometer. The values for temperature listed are those set on the VT controller. The sample temperatures were expected to be less than these values. Unless specifically mentioned, pulse sequences employing single-pulse Bloch decay measurements were used. ^{13}C NMR spectra were acquired with less than a 67° tip angle, while proton NMR spectra were acquired with less than a 25° tip angle in order to reduce the overdriving of the receiver amplifiers. High filling factor and narrow resonances provided strong NMR signals. All 2D MAS NMR reported were acquired in the 5 mm MAS probe at 100 °C with spinning speed of 8.5 kHz. Details of the acquisition parameters for the 2D NMR are listed in the text.

Three insoluble polymeric materials analyzed are listed in Table 1.

Discussion

In many cases, it is possible to acquire line-narrowed proton MAS NMR spectra of insoluble polymers at high temperature with minimal degradation by using a sealed sample and low flow rates of heating gas.[11] Under ideal spectrometer and sample conditions, the resolution in high-temperature proton MAS NMR spectra can be comparable to those obtained in dilute solution. Figure 1 shows a proton MAS NMR spectrum of poly(propylene) **I**, acquired without addition of a plasticizing solvent, that has excellent resolution with resolved 6.5 Hz resonances from spin−spin scalar coupling.

Narrow lines in the proton MAS NMR spectra of polymeric materials are obtained when the sample has significant mobility such that in the lab frame the neighboring nuclei are rapidly moving relative to each other. As mentioned earlier, when various parts of the molecules are librating independently and rapidly, nuclei do not stay fixed in relative 3-D space for long enough duration to interact and promote spin flips or spin exchange. The motion also reduces broadening caused by previously frozen variations in bond lengths, angles, and environments that are present in rigid materials. However, anisotropic bulk magnetic susceptibility (ABMS), if present in the polymeric system, is not averaged by MAS.[20,21] Its effects show up primarily as broader resonances in the proton NMR spectra. For example, proton MAS NMR spectra of aromatic polymers will have broader resonances compared to that of poly(propylene). When aromatic and carbonyl groups with anisotropic electronic environments surround nuclei, their net shielding is dependent on their vector sum with respect to the static magnetic field. Since MAS reorients each of the surrounding groups, the net shielding fluctuates, resulting in a broadened resonance. In dilute solutions, unlike polymers in a viscous state, each of the surrounding molecules has adequate motion for isotropic averaging during the data acquisition and hence their ABMS shielding effects are not observed.

Proton MAS (7 kHz) NMR spectra, acquired as a function of temperature, for a representative cross-linked insoluble amorphous polymer **II** that has a glass transition temperature of around 110 °C are shown in Figure 2. At room temperature the proton spectrum was broad and featureless, except for the presence of spinning sidebands. At 100 °C, the spectrum was narrower and spinning sidebands were not obvious. Further spectral narrowing occurred at 150 °C, and excellent resolution was observed at 200 °C. From the NMR data acquisition perspective, the system in this state at 200 °C is similar to that in solution. The proton and carbon NMR spectra acquired under these conditions are shown in Figure 3. The unreacted methacrylate groups, probably from the butanediol dimethacrylate cross-linker, can be detected in the proton MAS NMR spectra.

In a semicrystalline polymer or in a polymer that contains crystalline domains, it is necessary to break apart all the crystalline domains for a truly representative high-resolution NMR analysis. This can be achieved

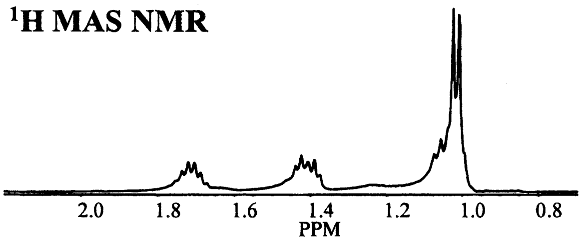


Figure 1. Proton 25 kHz MAS NMR of **I** at ~120 °C.

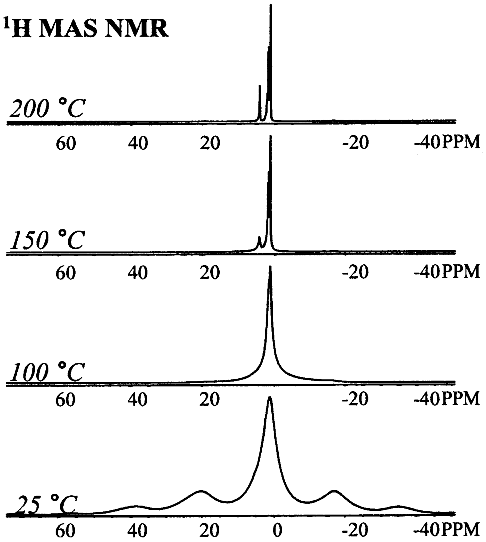


Figure 2. Proton 7 kHz MAS NMR spectra of **II**.

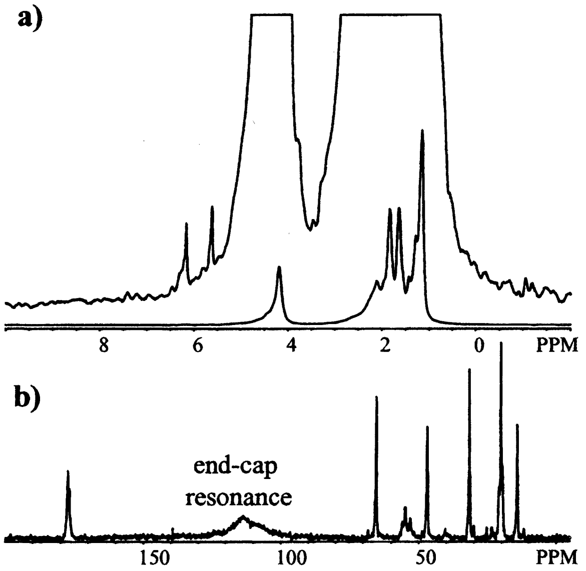


Figure 3. (a) Proton 7 kHz MAS NMR spectrum of **II** at 200 °C. The upper trace is an expansion to indicate the presence of unpolymerized methacrylate groups. (b) ^{13}C MAS NMR spectrum of the same sample under identical conditions.

either by addition of solvent or by acquiring data at temperatures close to the melting temperature of the crystalline domains. Degradation and undesired reactions can occur at temperatures significantly above the melting point of a polymer. We have found that polymer degradation can be minimized or made insignificant by using a relatively low variable temperature (VT) gas flow rate and sealing the MAS rotor.[11] A lower VT gas flow rate in the probes used in this study also leads to lower than the set temperature at the sample and a larger temperature gradient within the sample region of the rotor.[22]

The presence of crystalline or rigid components can be determined by comparing the shape of the spinning sidebands in the proton MAS NMR spectrum with that of the main resonances. For MAS speeds less than 10 kHz, the presence of a broad sideband underneath the narrower sideband is an indication of the presence of crystalline domains. For higher MAS speeds, as attained in 3.2 mm probes, if the shape of the spinning sideband is significantly different from that of the central band spectrum, most likely rigid domains are present at that given state and temperature. As an example, Figure 4 depicts ^{1}H (8.5 kHz) MAS NMR spectra of **III** acquired at 30 and 150 °C. The glass transition temperature of this methacrylate-terminated poly(caprolactone) was below room temperature, while the melting point was above room temperature. The rigid crystalline domains present at 30 °C had broader resonances and a larger CSA compared to that of the mobile amorphous component. The broad crystalline resonances were more clearly observed in the spinning sidebands than in the main isotropic resonances. At 150 °C, the crystalline rigid domains do not appear to be present. The significantly broad resonance between ^{1}H δ 40 and -30 ppm was the probe background from the static plastic components of the MAS module.

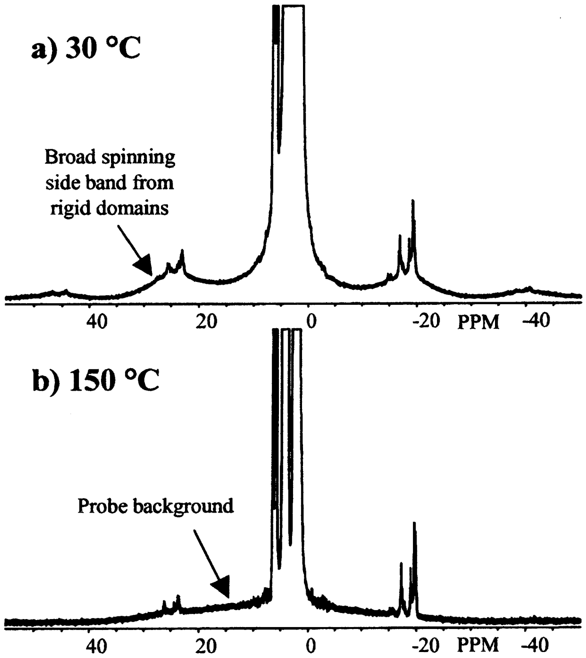
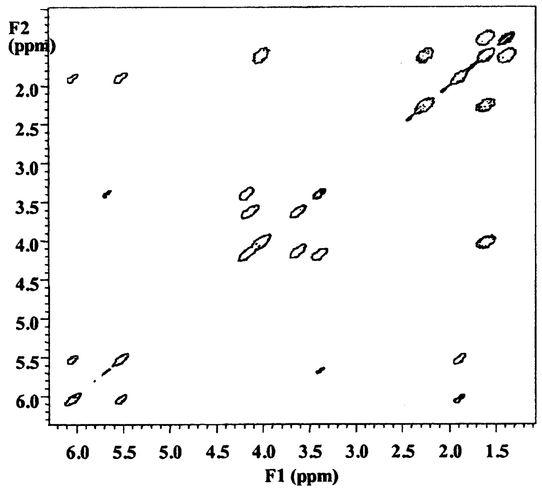


Figure 4. Proton 8.5 kHz MAS NMR spectra of **III** acquired at (a) 30 and (b) 150 °C using a 5 mm T3 Varian Chemagnetics MAS probe. The broad spinning sidebands in the 30 °C spectrum indicated the presence of rigid crystalline domains. The spectrum at 150 °C did not have the broad spinning sidebands. The broad underlying resonance between 40 and -30 ppm was from nonspinning parts of the probe module.

A number of 2D MAS NMR spectra that were acquired at 100 °C on **III** are reported below. The NMR pulse sequences provided by Varian in their VNMR software for solution NMR data acquisition were used without any further modification. Pulse sequences without gradients were employed since the MAS probe used did not have gradient capability. Homonuclear proton–proton correlations explored by MAS COSY and MAS TOCSY NMR spectra acquired at 100 °C are shown in Figure 5. The COSY spectrum was acquired for about 6 min using 1 scan, 0.34 s acquisition time, 256 increments, and a 1 s recycle delay, while the TOCSY spectrum was acquired for about 7 min using 1 scan, 0.17 s acquisition time, 64 increments, and a 2 s recycle delay. All expected proton–proton correlations were observed. Heteronuclear proton–carbon correlations were explored by both proton-detected and carbon-detected experiments.

Proton-detected MAS HMQC and MAS HSQC spectra acquired at 100 °C are shown in Figure 6. HMQC was acquired using 64 increments, 32 scans, 0.2 s acquisition time, and a 3 s recycle delay for about 4 h, while HSQC was acquired using 64 increments, 32 scans, 0.2 s acquisition time, and a 5 s recycle delay for about 3 h. The correlations from the major resonances were detected within a few minutes; however, observation of the methacrylate end group correlations shown in Figure 6 required the longer data acquisition time. Here, optimization of the null time for suppression of signals from protons attached to ^{12}C nuclei was necessary. The MAS HSQC data appeared to be noisier than the MAS HMQC data. This may be related to the presence of a larger number of pulses for a longer total duration in the HSQC pulse sequence compared to the HMQC sequence, providing more opportunities for errors, T_2 relaxation, and inadequate suppression of signals from protons attached to ^{12}C nuclei. The presence of temperature gradients in the sample and possible rf and magnetic field inhomogeneities may all contribute to phase errors during evolution of the spin coherences and to inadequate suppression of ^{12}C proton resonances.

a) COSY



b) TOCSY

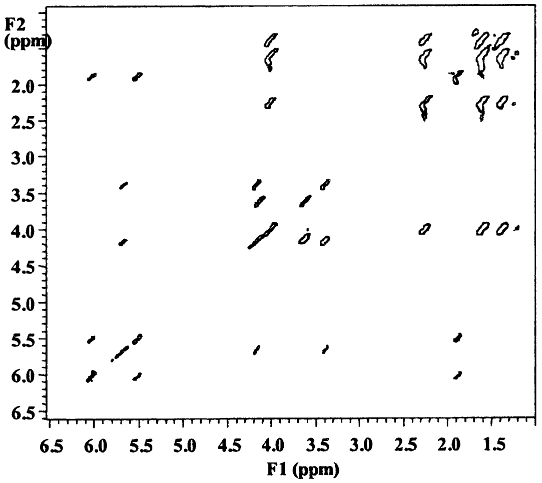


Figure 5. (a) MAS COSY and (b) MAS TOCSY of **III** acquired at 100 °C.

Carbon-detected 2D NMR spectra had less stringent rf pulse calibration requirements compared to the proton-detected 2D NMR spectra for single bond correlations. Edited MAS DEPT NMR spectra acquired at 100 °C with 16 scans, 0.09 s acquisition time, and a 5 s recycle delay for about 6 min are shown in Figure 7. Proton correlations from the major carbon resonances were detected in an 8 min MAS HETCOR[23−25] 100 °C acquisition using 64 increments, 0.05 s acquisition time, 2 s recycle delay, and the minimum of 4 transients required for phase cycling (data not shown). However, correlations for the minor resonances had intensities comparable with noise streaks from the major resonances. The MAS one bond C, H HETCOR acquired over a longer duration of about 35 min using 16 scans is shown in Figure 8a. Figure 8b shows a MAS long-range C, H (optimized for 10 Hz multiple bond) HETCOR that was acquired with 256 scans, 0.05 s acquisition time, 64 increments, and a 3 s recycle delay for about 14 h. The long-range correlations from the methacrylate end were stronger than those from the main-chain resonances of the polymer in this experiment. The three bond *J* couplings in the terminal methacrylate are expected to be between 8 and 10 Hz compared to the 2−5 Hz couplings in the poly(caprolactone), and the T_2 relaxation times are expected to be longer for the methylene end groups.

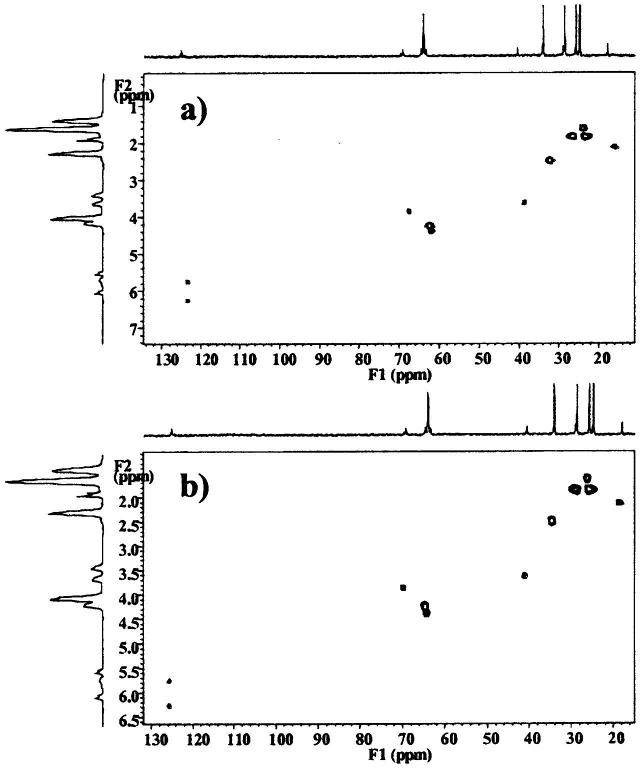


Figure 6. (a) MAS HMQC and (b) MAS HSQC of **III** acquired at 100 °C.

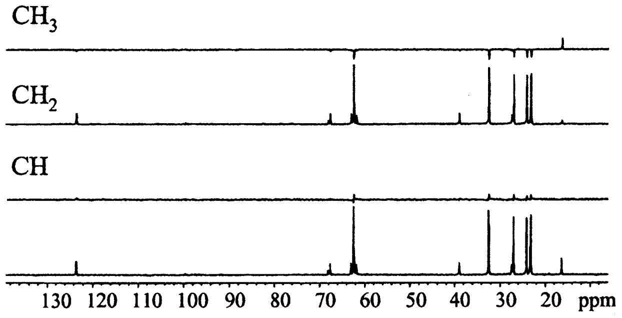


Figure 7. Dept NMR spectra of **III** acquired at 100 °C.

The ease of acquisition of these 2D NMR spectra confirms that, from the NMR data acquisition point of view, in this soft viscous state the material was similar to that in solution. In all cases, experiments that used fewer pulses and were of shorter duration yielded better results. Furthermore, multiple bond correlations were only observed via carbon-detected experiments. Attempts at acquiring reasonable HMBC spectra were not successful—here, the suppression of resonances from ^{12}C bound protons did not appear to be adequate compared to the signal strength of the long-range correlations.

Conclusion

We have demonstrated that well-resolved proton and carbon MAS NMR spectral resonances of insoluble polymeric materials can be acquired at high temperatures wherein the polymer is soft or viscous. Under the conditions under which narrow proton MAS NMR resonances were acquired, 2D NMR data could also be acquired. High filling factors and narrow resonances enable rapid data acquisition. MAS NMR at high

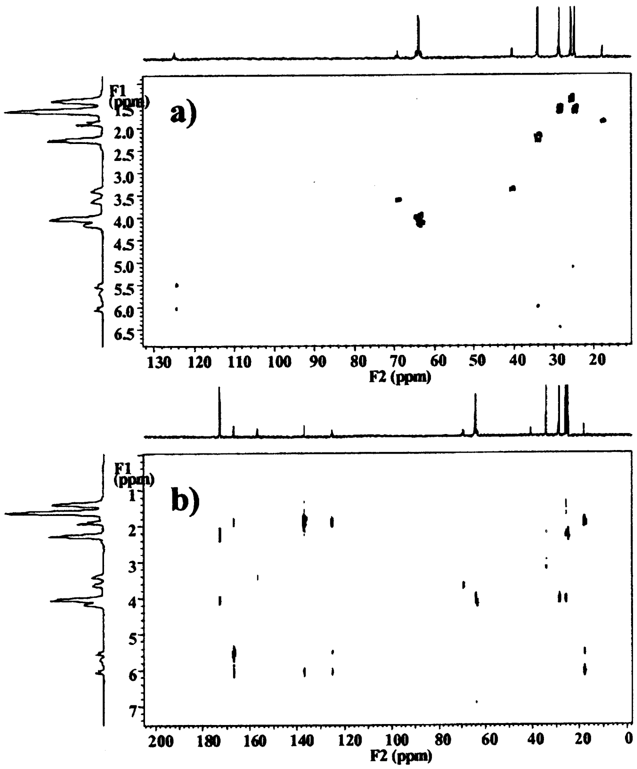


Figure 8. (a) MAS one bond C, H HETCOR of **III** at 100 °C and (b) MAS multiple bond C, H HETCOR of **III** at 100 °C.

temperatures can thus analyze insoluble polymers rapidly and routinely for identification and molecular composition.

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