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Polymer Degradation and Stability

Disclaimer

Analysis of Radiation Induced Degradation in FPC-461 Fluoropolymers by Variable Temperature Multinuclear NMR

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Abstract

Solid state nuclear magnetic resonance techniques have been used to investigate aging mechanisms in a vinyl chloride:chlorotrifluoroethylene copolymer, FPC-461, due to exposure to γ-radiation. Solid state ^{1}H MAS NMR spectra revealed structural changes of the polymer upon irradiation under both air and nitrogen atmospheres. Considerable degradation is seen with ^{1}H NMR in the vinyl chloride region of the polymer, particularly in the samples irradiated in air. ^{19}F MAS NMR was used to investigate speciation in the chlorotrifluoroethylene blocks, though negligible changes were seen. ^{1}H and ^{19}F NMR at elevated temperature revealed increased segmental mobility and decreased structural heterogeneity within the polymer, yielding significant resolution enhancement over room temperature solid state detection. The effects of multi-site exchange are manifest in both the ^{1}H and ^{19}F NMR spectra as a line broadening and change in peak position as a function of temperature.

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I. INTRODUCTION

Fluoropolymers are widely used in the chemical and aerospace industries due to their chemical and thermal stability, although substitution of fluorine atoms with other atoms or functional groups leads to a decrease in chemical resistance. Due to the inherent resistance of fluoropolymers to radiation and other forms of degradation (due primarily to the strength of the C-F bond – 485 kJ/mol compared to ~ 400 kJ/mol for C-H bonds), they find use in applications where thermal and radiation environments are harsh. As part of a larger lifetime assessment effort for fluoropolymers in general, we are studying the effects of γ-irradiation in a vinyl chloride:chlorotrifluoroethylene copolymer, FPC-461, used as a binder in some explosive formulations. The physical and mechanical properties of random block copolymers, such as FPC-461, depend on the ratio of each monomer block. For the formulation studied here, the ratio of vinyl chloride:chlorotrifluoroethylene is 0.6:0.4, as seen in Scheme 1.

The effects of ionizing radiation in polymers in general is well known to lead to competing crosslinking and chain scissioning reactions at dose-dependent rates and numerous methods exist to assess the effects of radiation, including solvent swelling, gel-permeation chromatography (GPC), and a variety of mechanical methods such as dynamic mechanical analysis.[1] Radiation effects on vinyl chloride polymers have been extensively studied and detailed mechanisms for dechlorination and production of stable alkyl radicals have been established.[2] Additional investigations into the effects of oxygen in the radiation process have lead to an understanding of the role of peroxyl radicals in the oxidation of the polymer chains to form ketones and alcohols. Similar studies on fluoropolymers have revealed comparable results.[3-5] For example, the effects of γ-irradiation on poly(chlorotrifluoroethylene) in Kel-F has been studied and a primary mechanism for chain scission through the carbon-carbon bond and a secondary C-F scission process along the polymer chain has been suggested.[6,7]

These observations, however, are often derived from electron spin resonance analysis of radical formation or GC/MS analysis of the volatile off-gasses. Nuclear magnetic resonance, on the other hand, provides an excellent means of investigating non-destructively the speciation and structural changes in the degraded polymer matrix. Solution state ^{19}F NMR provides high resolution structural information in non-protonated fluoropolymers that are not amenable to traditional ^{1}H NMR detection. The high sensitivity and wide chemical shift region of fluorine coupled with the capabilities of modern 3-channel spectrometers and probes to perform triple resonance ^{1}H/^{19}F/^{13}C experiments make it a powerful technique for polymer analysis.[8-10] Due to the chemically resistant nature of fluoropolymers, however, often they are not very soluble in traditional solvents, making solution state NMR difficult, if not impossible.

The application of solid state NMR spectroscopy to investigate polymer structure and dynamics is well documented.[11] NMR offers the advantage of being able to simultaneously probe structure and dynamics *in situ*, in controlled environments, on samples of various shapes. Changes in structure can be measured directly from changes in chemical shifts. In addition, changes in crosslink density can be inferred from the resulting effects on the polymer sequential dynamics directly measurable from the NMR data. Further, multinuclear NMR techniques can provide information about dynamics in both specific domains and the bulk system. Fluoropolymers do present a unique set of experimental difficulties. For example, both static and magic angle spinning (MAS) lineshapes are broadened by strong anisotropic interactions - i.e. the homonuclear ^{19}F-^{19}F dipolar coupling, heteronuclear ^{1}H-^{19}F dipolar coupling and chemical shift anisotropy (CSA). While CRAMPS is a well known method to improve static lineshapes in ^{1}H NMR,[12,13] the limited spectral window of CRAMPS methods prevents observing the entire relevant chemical shift range of fluorine. Magic angle spinning at very high speeds (>22 kHz) results in partial, but still not complete, averaging in the dipolar coupling,[14] but it has recently been shown that increased resolution can be obtained in ^{19}F MAS NMR by elevating temperature above T_g, often to very high temperatures (>300 ºC). Increases in segmental mobility in the polymer as well as the decreased structural heterogeneity lead to an averaging of the NMR lineshape, giving a narrow signal.[15] Moreover, the residual dipolar coupling that leads to spinning sidebands in solid state MAS spectra also undergoes motional averaging. While temperature elevation yields greatly increased spectral resolution, it was found that a combination of fast MAS and high temperatures is needed to achieve comparable resolution to that obtained in solution state spectroscopy.[15] This, of course, can cause concern if thermal degradation occurs at these temperatures in the timescale of the NMR experiment (minutes to hours).

In this paper the effects of γ-irradiation in FPC-461 will be investigated by solid state ^{1}H and ^{19}F NMR analysis using a combination of variable temperature and MAS NMR techniques. Due to a low temperature degradation process ($T_c \sim 160°C$), we concentrate on the resolution enhancements achievable at moderate temperatures ($T \leq 150°C$) and, since high spinning speeds can cause friction heating of the sample, moderate spinning speeds ($\nu_r \leq 17$ kHz).

II. EXPERIMENT

Materials

Samples of FPC-461 were obtained from Firestone Plastics, cold pressed into disks, and sealed in tubes containing either air or nitrogen environments. The samples were exposed to 1.2

MeV ^{60}Co irradiation at a rate of 5 kGray/hour for cumulative doses of 10, 100, 250, and 500 kGray. The irradiated samples were then placed either in the area of 5 mm NMR tubes in the center of the rf coil or stacked in 4 mm rotors for analysis.

Differential scanning calorimetry

DSC tests were run on a Perkin Elmer Diamond DSC equipped with an intracooler 2. Samples with a mass of approximately 5 mg were cut from pressed discs and placed in standard sealed aluminum pans. The instrument was previously calibrated against an indium standard and found to agree within 0.2^{o}C. Tests were run in multi-ramp sequences where the sample was first cooled to -20^{o}C, held at -20^{o}C for 2 minutes, ramped up to 320^{o}C at 20^{o}C/minute, held at 320^{o}C for 1 minute, ramped down to -20°C at 20^{o}C/minute, held at -20^{o}C for 2 minutes, then ramped up again to 320^{o}C at 20^{o}C/minute. The resulting heat flow was subtracted from that for an empty aluminum pan as the baseline correction. Glass transitions were calculated from the adjusted heat flow data using the instrument Pyris® software,[16] based on the temperature at which one half the change in the heat capacity has occurred as calculated from linear extrapolations of the heat flow curves above and below the transition.[17]

NMR

NMR experiments were performed at 11.7 T on a Bruker DRX500 with an operating ^{1}H frequency of 500.08 MHz and at 9.4 T on a Bruker Avance 400 with an operating ^{19}F frequency of 376.43 MHz. ^{1}H MAS spectra were obtained using a 4 mm H/X/Y DOTY CP/MAS probe for ^{1}H detection with 90° pulse lengths of 6 μs, recycle delays of 3 s and 16 scans. Magic angle spinning speeds of 12 kHz were generally used for the room temperature spectra. However, since the bearing air was used to raise the temperature, the spinning speed was limited by the temperature. When the temperature increased, more bearing pressure was required, resulting in slower spinning. For ^{19}F detection a 4 mm ^{19}F DOTY MAS probe was used with 90° pulse lengths of 3.5 μs, recycle delays of 4 s and 4 scans. Again, the MAS speed and temperature were interconnected, but in this case spinning speeds of 17 kHz were necessary to separate the spinning sidebands from the spectra, so lower temperatures were used in the variable temperature experiments.

III. RESULTS & DISCUSSION

The DSC procedure used provides information about the as-processed cold pressed sample as well as the sample at after it has been quenched to an equilibrium state. DSC curves of the pristine sample for both the initial scan and the second scan were similar in shape (seen in Figure 1), showing a single glass transition at a temperature of 55.4°C (first scan) and 52.5^{o}C (second scan). The similarity between the two scans indicates that the cold press procedure did not appreciably affect T_g. Also, at temperatures above approximately 150°C the heat flow curves become somewhat curved, possibly due to the polymer sample flow, degradation and/or off-gassing of volatiles in the DSC sample.

Initial ^{1}H magic angle spinning NMR spectra are shown in Figure 2 for a pristine sample and samples irradiated to 100 and 500 kGray in air. The pristine sample was characterized by a broad and relatively featureless ^{1}H MAS spectrum. After γ-radiation exposure, a narrow resonance at 6.9 ppm appeared and a decrease in the broad peaks at 4.5 ppm were observed. Many anisotropic interactions such as residual dipolar couplings have a spatial dependence that is averaged out with fast molecular motion, causing a narrowing of the NMR lineshape. The growth of the sharp, narrow peak and the respective decrease in the broad peaks indicates an increase in mobile species and decrease in immobile species in the polymer with radiation. The mobile phase was likely formed as a result of a reaction of alkyl radicals with oxygen to form reactive peroxyl radicals.[18] A decrease in spinning sideband manifold intensity with respect to the center peak with increasing dose for the broad peak indicates a decrease in the residual dipolar coupling between spins. As this coupling is an indication of molecular motion, the decrease represents an overall increase in motion, consistent with the theory of chain scission mechanism occurring in the sample, stiffening the network.

Though magic angle spinning provides significant resolution enhancements over static NMR spectroscopy, even greater resolution can achieved by heating the sample.[19] In Figure 3, ^{1}H MAS NMR spectra for the sample irradiated to 500 kGray in air are presented as a function of temperature. The spectra show little change up to ~ 75ºC. Above this temperature, a significant line narrowing occurred and two increasingly sharp peaks appeared as the mobility of the polymer increased above T_g. A dramatic decrease is linewidth at $T>T_g$ has been noticed in other systems [11,20] and corresponds to the onset of motion with a correlation time much less than the anisotropic interactions as the viscosity decreases. Often, these dramatic changes occur at 50-100°C above T_g. At higher temperatures, three separate major resonances can clearly be distinguished at 6 (assigned to oxygenated species formed as a result of the generation of peroxyl radicals), 4.4 (assigned to methine protons), and 2.2 ppm (assigned to methylene protons). At lower temperatures, an additional broad resonance is present at 0.5 ppm, assigned to methyl end groups. Although this signal does not grow significantly with temperature, at high temperatures it is dominated by the peak at 2.2 ppm, which has appeared due to the sudden increase in mobility of the methylene protons.

It is interesting to note that the peaks at 4.4 and 2.2 ppm did not narrow at the same temperature. The signal centered at 4.4 ppm was present at the room temperature spectrum and slowly sharpened as the temperature increased, while the resonance centered at 2.2 ppm did not appear until the temperatures reached 135°C. The different rates at which the peaks sharpened with temperature indicate a difference in residual anisotropic interactions, such as a likely increased H-H dipolar coupling of the methylene protons even with significant segmental motion in comparison with that of the methine proton. Evidence of chemical exchange is also present in the NMR spectra, particularly in the sharp signal at 6.9 ppm. A broadening of the peak was seen around 135°C and there was a gradual change in peak position from 6.9 to 6.0 ppm with increased temperature. Both of these features suggest multi-site chemical exchange is occurring on the timescale of the NMR experiment ($\tau_c \sim \mu s$ to ms). Due to the limited resolution obtained here, however, the exact nature of this exchange could not be determined.

^1H MAS NMR measurements at 150ºC, shown in Figure 4, show significant structural changes as a function of radiation. Specifically, the previously broad spectral features at 4.5 and 2.2 ppm now display much greater mobility and even dominate the sharp, mobile peak at 6.9 ppm seen as the sharp peak in the room temperature spectra in Figure 2. Though the appearance of two sharp peaks is evident in the 100 kGray sample, the peak at 6.9 ppm is not seen until the 500 kGray sample. The presence of these features at high temperature only suggests that there are multiple degradation mechanisms taking place. While one chain scission process produces species that are mobile even when the polymer is below its glass transition temperature, the other two major species do not exhibit high mobility until much higher temperatures. These results underscore the value of variable temperature NMR measurements in polymers whose T_g is above room temperature.

^{1}H MAS NMR results for samples irradiated in a nitrogen atmosphere are shown in Figure 5. Room temperature MAS experiments in Figure 5a were performed at spinning speeds of 12 kHz, while the higher temperature spectra of Figure 5b were obtained at 4.5 kHz. A small, sharp peak from a mobile species appears in the room temperature spectrum at 500 kGray similar to the mobile peak in the sample irradiated in air, possible due to O_2 impurities in the N_2 atmospheres of H_2O impurities in the polymer matrix. The changes in the room temperature spectra hint at some structural changes, with even more structure appearing in the high temperature spectra. In this case the resolution is still not great enough to accurately distinguish individual signals from degradation products. At this point, however, it can be said that a certain degree of degradation is occurring in the vinyl chloride region of FPC-461 at doses lower than 100 kGray.

^{19}F MAS NMR was used to determine the effects of radiation on the chlorotrifluoroethylene block. Results similar to the high temperature ^{1}H results are seen in the variable temperature ^{19}F NMR spectra of 500 kGray (air) samples shown in Figure 6. First there is a general decrease in the relative intensity in the spinning sidebands indicating an overall decrease in the residual anisotropic interactions as the segmental mobility increases with temperature. Here, the sharpening of the signals as the temperature increased revealed an increase in the resolution of the resonances centered at 109 (assigned to $\text{-CF}_2\text{CH}_2\text{C}\underline{\text{F}}_2\text{CF}_2\text{CFCl-}$) and 119 ppm (assigned to either $\text{-CH}_2\text{CF}_2\text{C}\underline{\text{F}}_2\text{CF(CF}_3\text{)CH}_2\text{-}$ and $\text{-CH}_2\text{CF}_2\text{C}\underline{\text{F}}_2\text{CFClCH}_2\text{-}$ or mixtures thereof), while the shoulder centered at 123 ppm (assigned to $\text{-(CF}_2\text{)}_n\text{-}$) appears to decrease with temperature. A fourth peak at 127 ppm (assigned to either $\text{-CF}_2\text{C}\underline{\text{F}}\text{ClCH}_2\text{-}$ and $\text{-CH}_2\text{CF}_2\text{C}\underline{\text{F}}_2\text{CF}_2\text{CH}_2\text{-}$ or mixtures thereof) was also observed to grow in at higher temperatures. (The initial assignments of these peaks were made based on previously published high resolution spectral analysis.[12]) Like the ^{1}H variable temperature MAS spectra, a change in chemical shift in some of the signals was observed. For example, a small downfield shift was observed in the signals 119 ppm and 127 ppm in addition to the line narrowing. It is likely that these changes were caused by either by multi-site exchange between different stereoisomers or by the differences in dipolar couplings of the assigned groups leading to different motional properties at the given temperatures.

In contrast to the clear evidence of degradation by chain scission in the vinyl chloride region of the polymer, negligible effects are seen in the ^{19}F spectra for both air (Figure 7) and nitrogen (Figure 8) samples. This is not surprising, given the extremely large bond strength of the C-F bond (485 kJ/mol). Although higher spinning speeds were used here in comparison with the ^{1}H data, lower temperatures were used. In previous variable temperature experiments with fluoropolymers, significant resolution enhancements were observed at comparable spinning speeds and temperatures to those used here, and even higher resolution was achieved at temperatures > 200ºC.[15] Performing ^{19}F MAS experiments at such elevated temperatures and exceedingly high spinning speeds must be performed with cautions given the possibility of thermal degradation and the temperature limits of the probe and melting points of the rotor and cap material. In the case of FPC-461, temperatures higher than 150°C are not desirable due to the degradation observed at higher temperatures in the DSC curves in Figure 1.

IV. CONCLUSIONS

NMR spectroscopy has been used to investigate the effects of γ-irradiation in the fluoropolymer FPC-461. Through a combination of magic angle spinning and variable temperature solid state NMR, significant degradation was seen in the vinyl chloride region of the polymer by ^{1}H NMR, while negligible changes were seen in the chlorotrifluoroethylene block using ^{19}F NMR. The additional effects of oxygen in the degradation processes in the vinyl chloride region were seen when comparing the samples irradiated in air and nitrogen environments. Though a detailed investigation of thermal degradation is underway for FPC-461, degradation effects have been seen after holding the polymer at 150ºC for extended periods of time. Degradation around 160°C was confirmed by DSC analysis, indicating that higher temperature NMR analysis is not possible without further damaging the sample.

A complete analysis of radiation and thermally induced degradation pathways using a combination of solution state NMR, GC/MS, and mechanical analysis is underway to determine the exact nature of the chemical degradation. High resolution solution state analysis is necessary for complete spectral assignment of both the ^{19}F and ^{1}H spectra. Triple resonance (^{1}H/^{19}F/^{13}C) experiments which allow for ^{19}F-^{1}H decoupling have proven to be a useful tool for complete characterization of fluoropolymers,[9] and are planned in the complete analysis of degradation of FPC-461. The results of the data presented here in conjunction with a full suite of solution state NMR spectra and GC/MS results will allow for complete structural elucidation of the degradation products and the corresponding off-gassing products.

VII. ACKNOWLEDGEMENTS

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Scheme 1 Molecular structure of one FPC-461 unit.

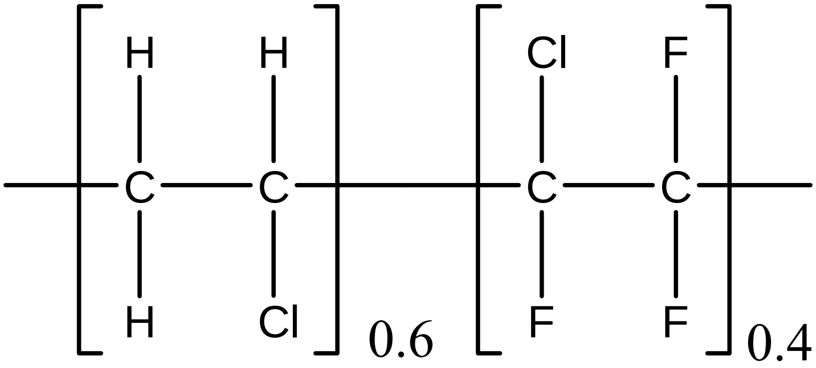

Figure Captions

Figure 1. DSC curves for pristine FPC-461. The curve for the first heat has been vertically shifted by 2 mW. The glass transition temperatures on each curve are noted with a tic mark.

Figure 2. ^{1}H MAS NMR spectra of FPC-461 irradiated 0, 100, and 500 kGray in air at room temperature with MAS speeds of 13 kHz. Spinning sidebands are indicated by a star (*).

Figure 3. Variable temperature ^{1}H NMR spectra of FPC-461 irradiated to 500 kGray in air. The spectra were obtained under MAS conditions at the spinning speeds indicated at the side.

Figure 4. ^{1}H MAS NMR spectra of FPC-461 irradiated 0, 100, and 500 kGray in air at 150°C with MAS speeds of 4.5 kHz.

Figure 5. ^{1}H MAS NMR spectra of FPC-461 irradiated 0, 100, and 500 kGray in nitrogen at (a) 25°C, spinning at 12 kHz and (b) 150°C, spinning at 4.5 kHz. Spinning sidebands are indicated by a star (*).

Figure 6. Variable temperature ^{19}F MAS NMR spectra of FPC-461 irradiated to 500 kGray in air. The spectra were obtained under MAS conditions at 17 kHz spinning speeds. Spinning sidebands are indicated by a star (*).

Figure 7. ^{19}F MAS NMR spectra of FPC-461 irradiated 0, 100, and 500 kGray in air at (a) 25°C, and (b) 95°C. Both experiments were performed at 17 kHz MAS speeds. Spinning sidebands are indicated by a star (*).

Figure 8. ^{19}F MAS NMR spectra of FPC-461 irradiated 0, 100, and 500 kGray in nitrogen at (a) 25°C and (b) 95°C. Both experiments were performed at 17 kHz MAS speeds. Spinning sidebands are indicated by a star (*).

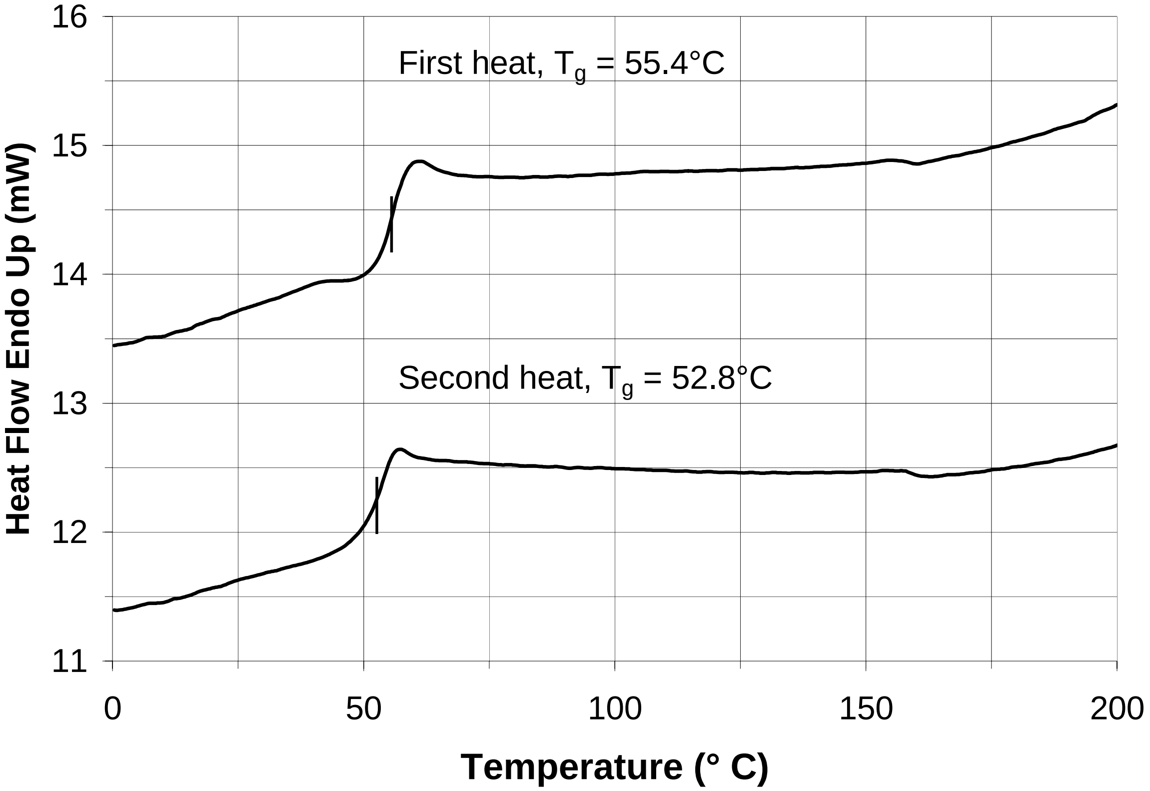

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Figure 1

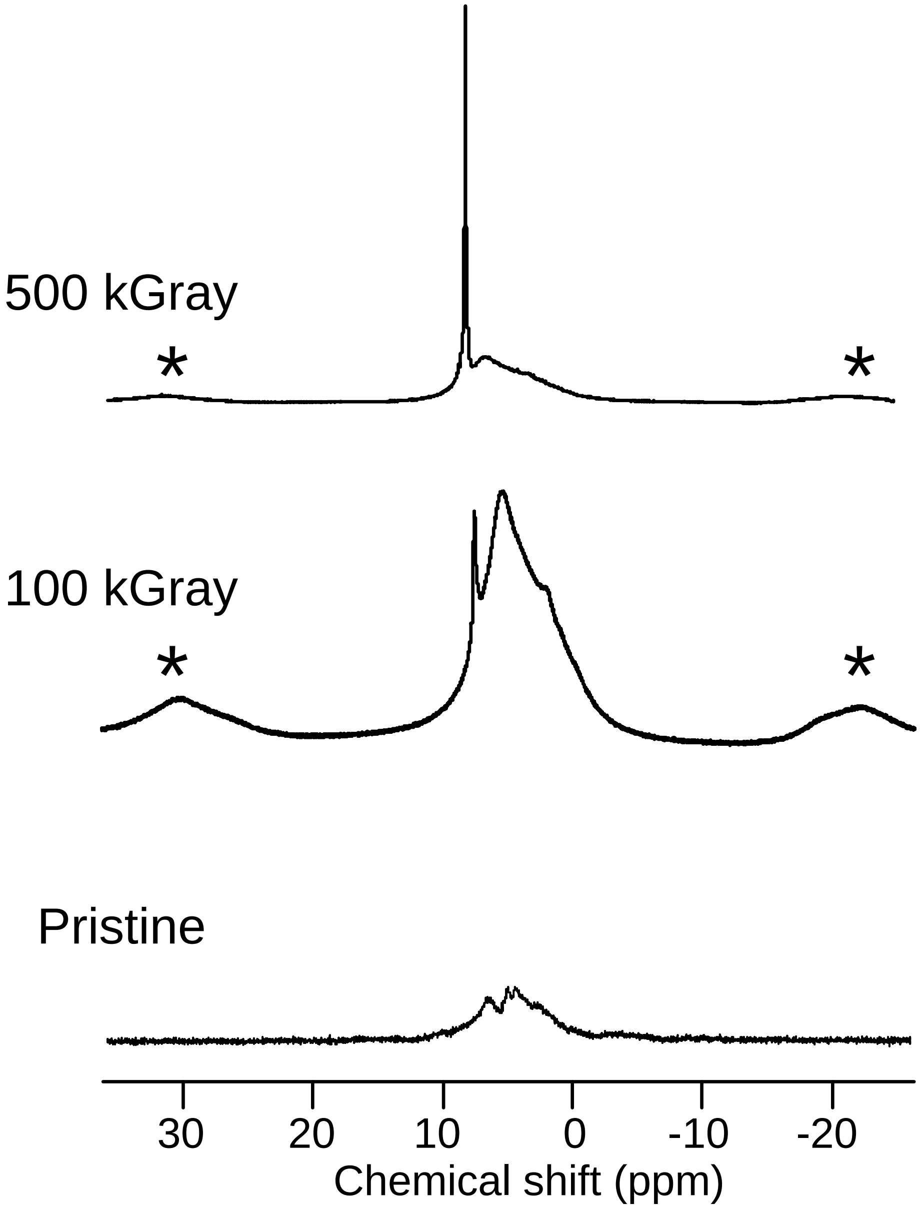

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Figure 2

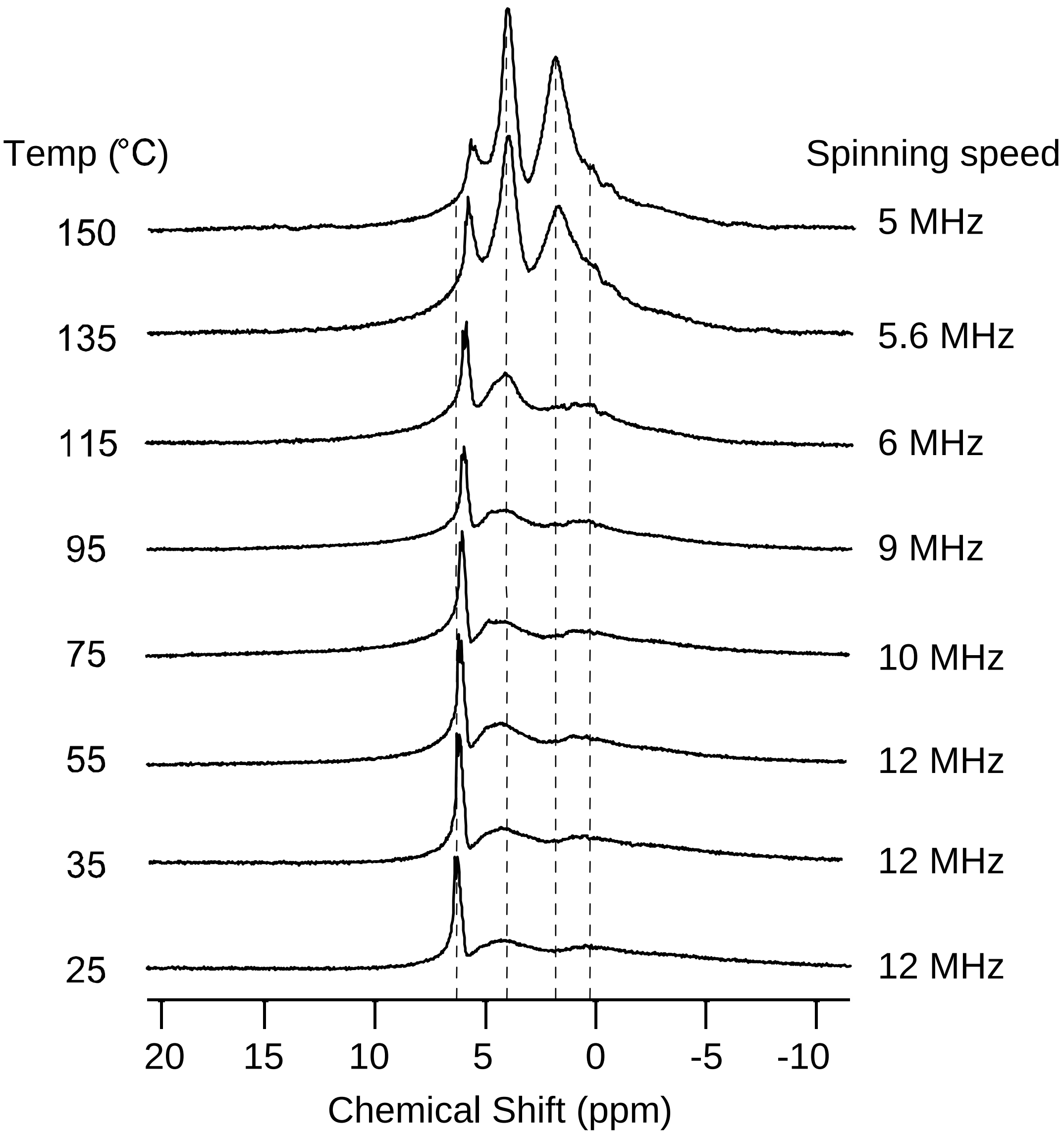

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Figure 3

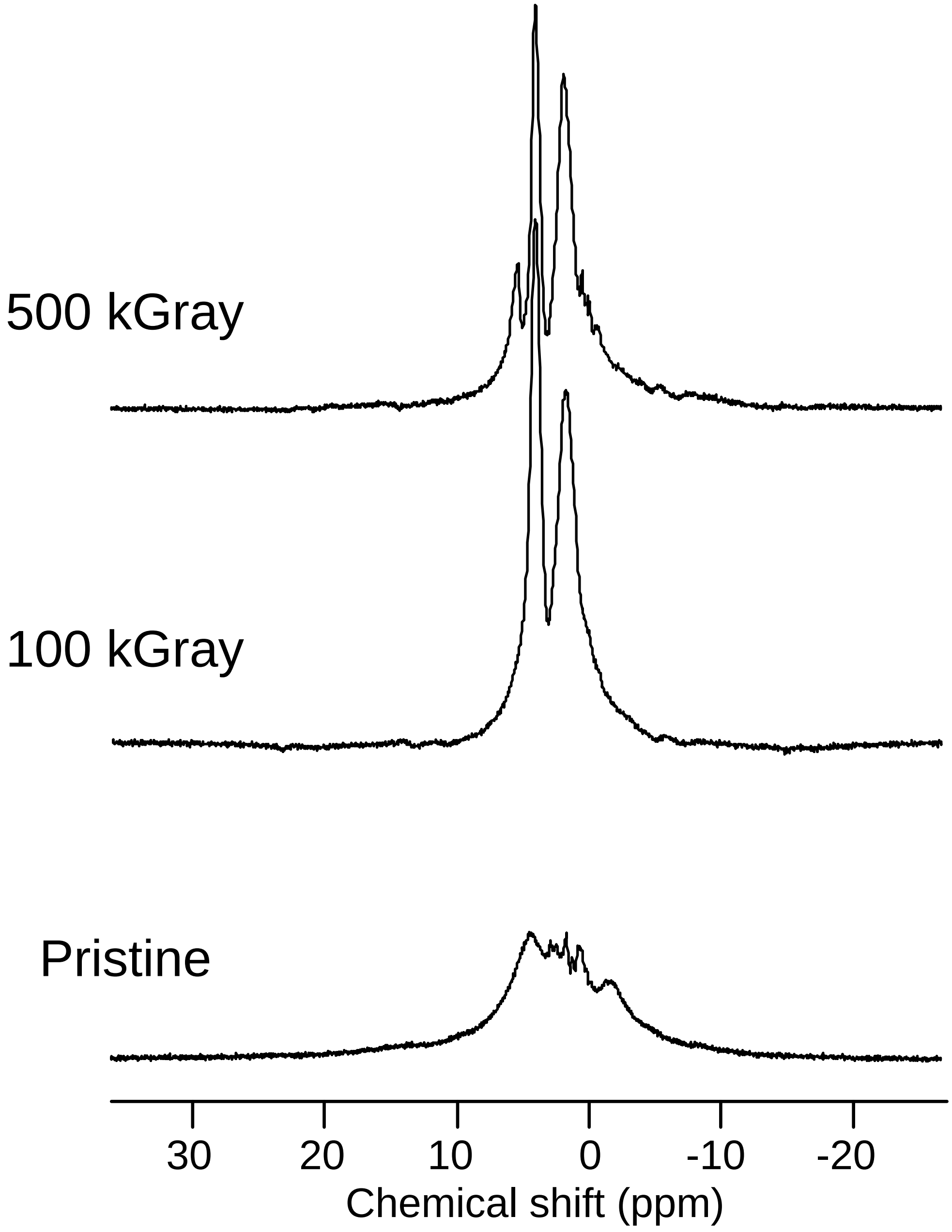

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Figure 4

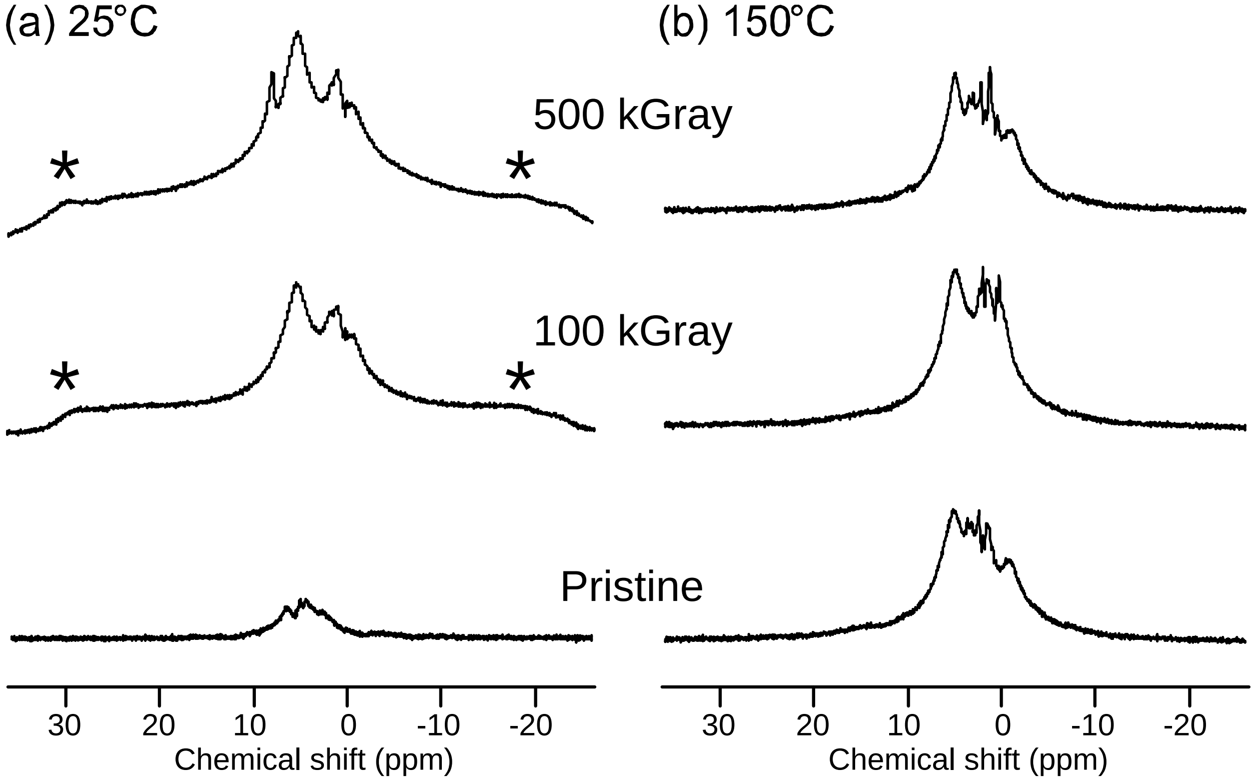

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Figure 5

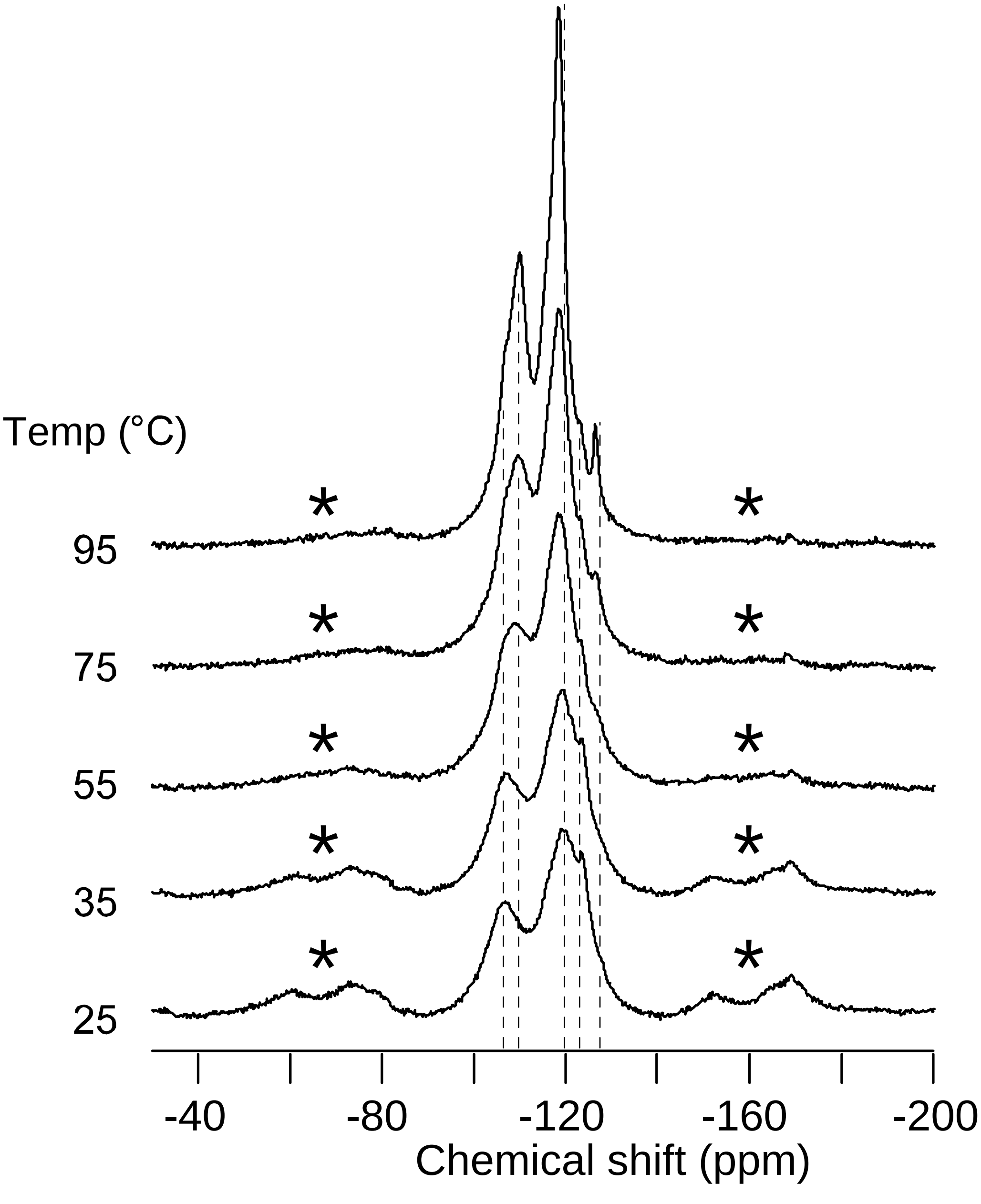

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Figure 6

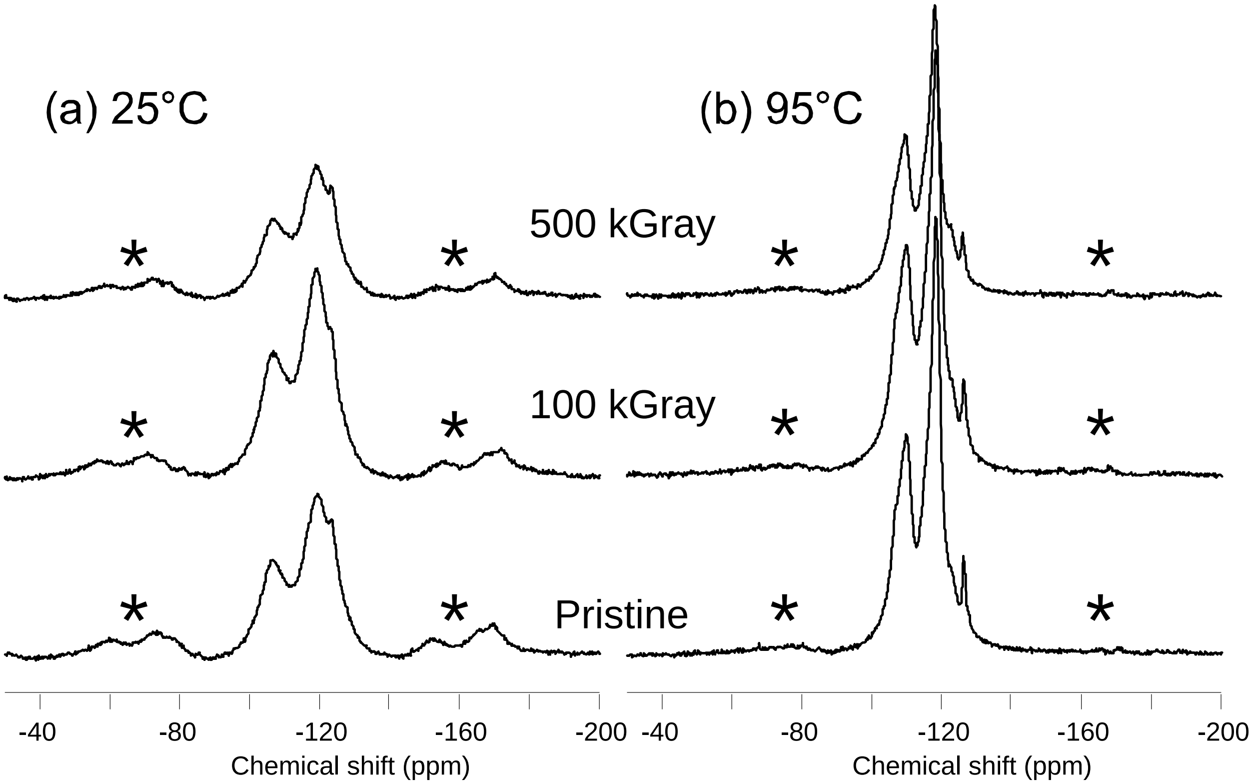

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Figure 7

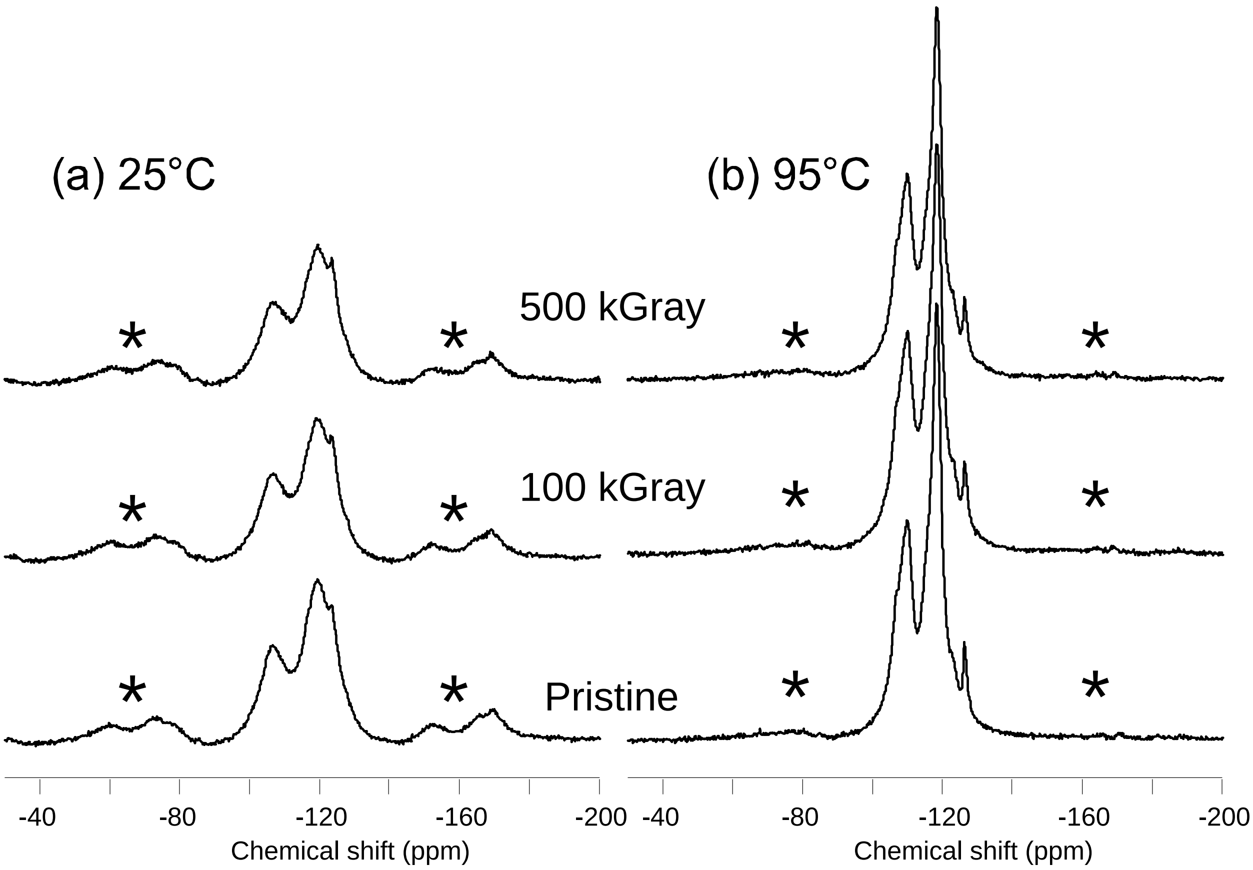

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Figure 8