**Synthesis and Solid-State NMR Characterization of 13C- and 15N-labelled N-Methylphthalimide: A Model Compound for Studying Polyimides**

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High-resolution solution and solid-state NMR techniques have been used for a number of years to characterize biological and polymeric systems. However, these techniques only observe the isotropic chemical shift (5) value and ignore the valuable information it may be obtained from the anisotropic 5 tensor, which is sensitive to the structural and chemical environment. Within the last ten years, researchers have done a great deal of work determining \[^1^H, ^{13}C\] chemical shifts for nitrogen and carbon nuclei. Even though the 5 tensor, which is sensitive to the structural and chemical environment, has been used for a number of years to characterize biological and polymeric systems, little has appeared regarding the magnitude and orientation of the \[^{13}C\] chemical shift tensor for some model imides. Its application to synthetic polymers has been limited.

The Gabriel method allows preparation of imide derivatives from methyl iodide in good yields. The \[^1^H\] T\(_s\)s were approximately 65-78 s for all protons, including the aromatic protons. \[^{13}C\] CP/MAS NMR spectra of the model N-methylphthalimide showed a number of peaks for the aromatic carbons which may be due to differences in crystal packing. However, the \[^{15}N\] spectra show a single peak (\(\delta_{15N} = 119.7\) ppm) for imides 2 and 3.

\[^{13}C\] and \[^{15}N\] static powder spectra for the model imides are shown in Figures 1 and 2, respectively. For both figures the upper spectrum (a) corresponds to the singly labelled material, while the lower spectrum (b) corresponds to the doubly labelled compound. For all spectra presented the spectrum is in ppm, with the left peaks corresponding to lower ppm values. A Kaiser digital filter function was applied to the FID prior to Fourier transformation, with the \(\alpha\) parameter set to 1 and the cutoff value varied between 3-5 ms. Even though the imides were labelled with equal amounts of isotope, approximately 500 transients were taken for the \[^{15}N\] spectra to achieve a signal-to-noise ratio of 100, while 32 transients for \[^{13}C\] were taken to achieve the similar signal-to-noise. This probably reflects the differences in sensitivity between the two nuclei due to changes in the probe's tuning characteristics in going from 50 to 20 MHz.

One of the initial pursuits in synthesizing the singly \[^{13}C\] labelled material was to obtain the unperturbed \[^{13}C\] CSA spectrum for use in simulating the \[^{15}N, ^{13}C\] dipolar-coupled spectrum. However, the presence of the 99% naturally abundant \[^{15}N\] isotope clearly distorts the spectrum due to its dipolar coupling and large quadrupolar moment (I=1 spin). Although it is possible to simulate \(I=1/2\) spins coupled to quadrupolar nuclei, such a study is beyond the scope of this work.

Figure 2 shows the \[^{15}N\]-labelled and the \[^{15}N, ^{13}C\] doubly labelled material. A classic anisotropic CSA spectrum was obtained for the \[^{15}N\]-labelled compound, and from computer simulation the tensor elements were found to be 56.4 ppm, 65.3 ppm, and 3.3 ppm for \[^{15}N\] acquisition, while a mixing pulse of 2 and 50 ms acquisition were used for both nuclei. A recycle delay of 210 s, corresponding to 3-4 \[^1^H\] T\(_s\), was used for observation of the \[^{13}C\] nuclei. The same parameters were used to acquire static spectra except for the spinning rate, which was set to zero. \[^1^H\] T\(_s\)s were determined by monitoring the nitrogen or carbon signal using a 100-180-180-180-CP inversion-recovery pulse sequence. Chemical shift anisotropy (CSA) spectra were simulated using the POWFIT program developed by Dr. J. G. Oss. All simulations were done MicroVax SI00.

A typical procedure for the preparation of an \[^{15}N\] NMR sample involves reagent grade methylphthalimide (DMF) reagent grade as received. A typical procedure for the preparation of an N-methylphthalimide is as follows: A clean, dry flask was charged with equal molar amounts of \[^{15}N\] potassium phthalimide and methyl iodide followed by enough N,N-dimethylformamide (DMF) to give a mixture that was 15 to 20 % solids by weight. The flask was submerged in a preheated oil bath at \(-60^\circ\)C for 2 to 3 hours. The cooled reaction mixture was poured into rapidly stirring water (10 times its volume), the precipitate collected and recrystallized from aqueous ethanol (70 to 85 % yield).
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REFERENCES


