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

W. L. Jarrett, C. G. Johnson, L. J. Mathias

13a. TYPE OF REPORT
Technical

13b. TIME COVERED
FROM 6/1/93 to 31/94

14. DATE OF REPORT (Year, Month, Day) 7/15/94

15. PAGE COUNT

16. SUPPLEMENTARY NOTATION
See attached.

17. COSATI CODES

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

19. SECURITY CLASSIFICATION OF THIS PAGE Unlimited

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT

21. ABSTRACT SECURITY CLASSIFICATION

22a. NAME OF RESPONSIBLE INDIVIDUAL
Lon J. Mathias

22b. TELEPHONE (Include Area Code) 601-266-4871

22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted.
Solid-state CP/MAS NMR spectra were obtained on a Bruker 3L-200 equipped with a Bruker MAS probe operating at 50.32 and .287 MHz for $^{13}$C and $^{15}$N, respectively. Powdered samples were used in fused zirconia rotors fitted with Kel-F caps and spun with air, with rotation rates of 4 to 5 kHz for carbon MAS and 2 to 3 z for nitrogen MAS. The $^{13}$C spectra were referenced to external amantane (29.5 ppm), while $^{15}$N spectra were referenced downfield m external glycine (0 ppm). The $^1$H 90° pulse was 4.5 $\mu$s for $^{13}$C acquisition and 6.0 $\mu$s for $^{15}$N acquisition, while a mixing pulse of 210 and 50 ms acquisition were used for both nuclei. A relay delay 210 s, corresponding to $-3^h$ $^1$H $\tau_s$, was used for observation of th nuclech. The same parameters were used to acquire static spectra except for the spinning rate, which was set to zero. $^1$H $\tau_s$ were determined by monitoring the nitrogen or carbon signal using a $^{180}_{\circ}$$-90_\circ$-CP inversion-recovery pulse sequence.

Chemical shift anisotropy (CSA) spectra were simulated using POWFIT program developed by Dr. T. G. Oas.$^3$ All simulations were done MicroVax 3100.

Potassium phthalimide, $[^{13}$C] methyl iodide, and methyl iodide were obtained from Aldrich Chemical Company and used without purification. Dimethylformamide (DMF) was reagent grade used as received.

A typical procedure for the preparation of an N-methylphthalimide is as follows: A clean, dry flask was charged with an equimolar 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).

**RESULTS AND DISCUSSION**

The Gabriel method allows preparation of imide derivatives from methyl iodide in good yields. The $^1$H $T_2$'s were approximately 65-78 s for all protons, including the aromatic protons. $^{13}$C CP/MAS NMR spectra of the model N-methylphthalimides showed multiple peaks for the aromatic carbons which may be due to differences in crystal packing. However, the $^{15}$N spectra show a single peak ($\delta_{ref} = 119.7$ 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 x axis is in ppm, with upfield shifts 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 static 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 as well as changes in the probe's tuning characteristics in going from 50 to 20 MHz.

One of the initial purposes in synthesizing the singly $^{15}$C labelled material was to obtain the unperturbed $^{15}$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 $^{13}$C-$^{15}$N doubly labelled material. A classic anisotropic CSA spectrum was obtained for the $^{15}$N-labelled compound, and from computer simulation the tensor elements $\delta_1$, $\delta_2$, and $\delta_3$ were found to be 56.4 ppm, 126.3 ppm, and 177.3 ppm, respectively. These values of the $\delta$ tensor were used for simulating the $^{15}$N-$^{13}$C dipolar coupled spectrum. A comparison of the experimental and simulated spectra is shown in Figure 3. The value of the dipolar coupling constant (872 Hz) indicates that the N-CH$_2$ bond distance is 1.52 Å. The polar coordinates $\alpha$ and $\beta$, which describe the orientation of the $^{15}$N-$^{13}$C bond vector with respect to the principal axis of the chemical shift tensor, were 68.0° and -45.9°, with the $\delta_3$ tensor element aligned approximately along the N-CH$_2$ bond (Figure 4). For our analysis, the $\delta_2$ tensor was assumed to be perpendicular to the imide plane; similar assumptions have been used for the amide moiety of polyamides.$^3$

**CONCLUSION**

A procedure has been developed for incorporating $^{15}$N and $^{13}$C isotopic labelling into N-methylphthalimide, a model imide. From solid-state $^{15}$N NMR spectroscopic methods the values and orientation of the $\delta$ shift tensor with respect to the N-CH$_2$ bond as well as the N-CH$_3$ bond length have been determined. Future work concerning the determination of the $\delta$ tensor for some model polyimides is in progress.
ACKNOWLEDGEMENTS

The authors would like to acknowledge the Office of Naval Research for providing funds for the purchase of the MSL-200 spectrometer and Dr. Terry Oas for providing the POWFIT program.

REFERENCES


