CONF-960376--5

SAND96-0340C

# Characterization of Polyxylylenes with Solid State $^{13}$C Nuclear Magnetic Resonance Spectroscopy.

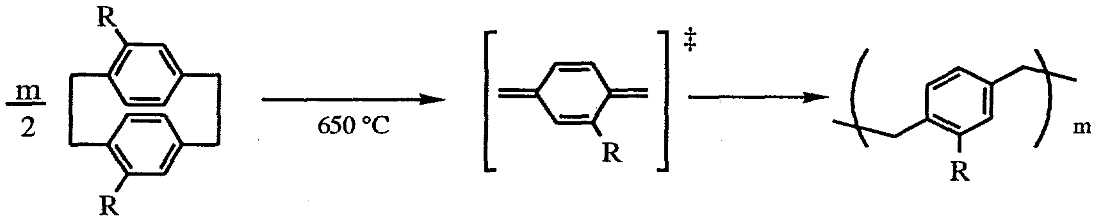
Douglas A. Loy[†]*, Roger A. Assink[†], Gregory M. Jamison[†], W. Frere McNamara[†], S. Prabakar[‡], and Duane A. Schneider[†].

[†] Sandia National Laboratories, Albuquerque, NM 87185-1407
[‡] Advanced Materials Laboratory, University of New Mexico, Albuquerque, NM 87106

RECEIVED
FEB 12 1996
OSTI

## Introduction.

Polyxylylenes are an important class of thermoplastics used as encapsulants for electronic devices.[1] They are most conveniently prepared from [2.2]paracyclophanes by a vapor deposition polymerization technique known as the Gorham Process (Scheme 1).[2] In this process, [2.2]paracyclophane is sublimed into a furnace where it is thermally cleaved into two equivalents of xylylene monomer.[3] The end result of the Gorham process is a solvent-free film composed of linear, highly crystalline, high molecular weight polymer.[4] Polyxylylene and chloro-substituted polyxylylenes are crystalline enough to result in insolubility up to the melt temperatures (300 °C). Solvent and chemical resistance, in combination with the ability of vapor deposition polymerization to evenly coat irregular surfaces with polymer, makes polyxylylenes a valuable class of encapsulants.



Scheme 1. Formation and polymerization of xylylene monomers **1-5** from paracyclophanes.

These same characteristics also make polyxylylene and poly-haloxylylenes difficult to characterize by analytical techniques, such as solution nuclear magnetic resonance (NMR) spectroscopy. Solid state $^{13}$C Cross Polarization Magic Angle Spinning (CP MAS) NMR spectroscopy is a convenient and routine alternative to x-ray diffraction techniques used to characterize molecular structure of both types of materials.[5] We became interested in structurally characterizing polyxylylene materials as part of our study of fullerene-xylylene copolymers.[6] It was noted during this investigation that $^{13}$C NMR spectra had not been previously reported for any of the polyxylylenes. Here we describe the preparation of polyxylylene **P1**, poly-2-ethylxylylene **P2**, poly-2-chloroxylylene **P3**, polydichloroxylylene **P4**, and poly($\alpha$, $\alpha$, $\alpha'$, $\alpha'$-tetrafluoroxylylene)[7] **P5** (Figure 1) by the pyrolysis of their respective [2.2]paracyclophanes and their characterization using solid state $^{13}$C CP MAS NMR spectroscopy.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

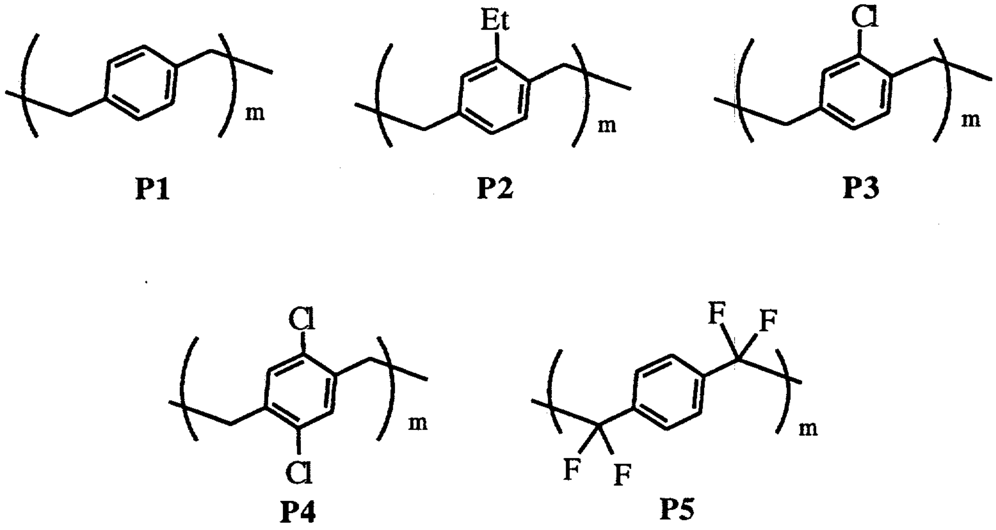


Figure 1. Polyxylylenes (**P1-P5**) prepared by pyrolysis of [2.2]paracyclophanes and characterized by solid state $^{13}C$ NMR spectroscopy.

## Experimental

### General.

[2.2]paracyclophane, dichloro[2.2]paracyclophane, tetrachloro[2.2]paracyclophane, and diethyl[2.2]paracyclophane, were obtained from Union Carbide and used as received. $\alpha$, $\alpha$, $\alpha'$, $\alpha'$-Octafluoro[2.2]paracyclophane was obtained from Professor William R. Dolbier, Jr. at the University of Florida. Infrared analyses of the films were performed in a Perkin-Elmer 1750 Fourier Transform Infrared spectrometer. Solution $^{13}C$ NMR spectra of [2.2]paracyclophane precursors were obtained in deuterochloroform with a Bruker AM 200 MHz spectrometer. Solid state $^{13}C$ NMR spectra were obtained at 50.19 MHz with a Chemagnetics console interfaced to a Nicolet 1280 data station. Samples were spun between 4-6 kHz. Chemical shifts are relative to a hexamethylbenzene standard set to 17.2 ppm for the methyl carbons. Signal precision in the solid state NMR spectra was ± 0.1 ppm for most resonances. Spinning side bands in the spectral data are abbreviated as *ssb*. Interrupted decoupling experiments were performed by inserting a 60-90 μs delay between cross polarization and acquisition.

### Polymer Synthesis.

Paracyclophanes were sublimed (or distilled) into an evacuated quartz tube heated to 650 °C (0.5-1 mm Hg) and the xylylene monomers generated were condensed/polymerized on glass at either room temperature, cooled to 0 °C with an ice bath or cooled to -78 °C with a dry ice-acetone bath. The films could be peeled from the glass and were dried under dynamic vacuum for 18 hours at room temperature. Thick films were opaque and generally white, though polyxylylene films were occasionally tinted grey-green. Thin films prepared at room temperature were transparent.

### Results.

Thermolysis of paracyclophanes in a flow-through pyrolysis apparatus afforded thin films of polyxylylenes. In all cases, some of the monomer was converted into a film of carbon lining the inside of the quartz tube; the majority passed through the hot zone of the tube to condense and polymerize on glass surfaces. Yields of the polymers based on monomer ranged between 20-50% and were based only on material that condensed on the inner surface of a receiving flask placed in a controlled temperature bath. Flexible polyxylylene films were peeled from the glass surface on which they had formed and were characterized by infrared and $^{13}C$ CP MAS NMR spectroscopies. The infrared spectra of the polyxylylenes **P1-P4** are similar to reported spectra.[1c]

The solution $^{13}C$ NMR spectrum of [2.2]paracyclophane (Figure 2A) was obtained to provide a reference for the solid state $^{13}C$ CP MAS NMR spectra of the insoluble polyxylylenes. The solution $^{13}C$ NMR spectrum was composed of three signals representing the substituted (139.6 ppm) and unsubstituted (133.0 ppm) aromatic and benzylic methylene (35.7 ppm) carbons.[8] The solid state $^{13}C$ CP MAS NMR spectrum of polyxylylene **P1** (Figure 2B) also displayed three analogous, but somewhat broad peaks for the substituted (140 ppm) and unsubstituted (133 ppm) aromatic and benzylic methylene (40 ppm) carbons. No end-group methyls (23 ppm) were observed in any of the polyxylylenes, indicating that the polymers were not oligomeric.

Interrupted decoupling experiments with **P1** were used to confirm the peak assignments of the aromatic carbons (Figure 3). With the insertion of a 90 μs delay between cross polarization and acquisition, the carbon nuclei are exposed to the dipole interactions of the surrounding protons. Resonances of carbon nuclei directly bonded to a proton are broadened and attenuated more than the resonances of carbon nuclei not directly bonded to a proton. The benzylic methylene at 40 ppm disappeared entirely and the peak (*C*H aromatic) at 128.8 ppm was sharply attenuated. The resonance at 140 ppm (*C* aromatic) was attenuated far less than the other two peaks and became the dominant peak in the spectrum. In some samples of polyxylylene, shoulders on the aromatic peaks were observed that were determined to be due to entrapped paracyclophane. Soxhlet extraction of polyxylylene (**P 1**) with benzene recovered considerable [2.2]paracyclophane (14.2% by weight). In addition, when α, α'-$^{13}C$ enriched polyxylylene was washed with benzene and re-examined by $^{13}C$ CP MAS NMR, the subsequent spectrum of the polymer revealed that the shoulder on the benzylic carbon resonance had disappeared.

The solid state spectra for the functionalized polyxylylenes **P2-P4** were similar to that of the unsubstituted polyxylylene **P1** with broad overlapping resonances in the aromatic region and the benzylic methylene appearing near 40 ppm. The ethyl-substituted **P2** also displayed additional carbon peaks at 24 and 16 ppm. Interrupted decoupling generally eliminated the benzylic methylene completely while the attenuation of peaks in the aromatic region resulted in either simplification of the spectra or the appearance of previously obscured peaks (**P3 & P4**). Two aromatic carbon resonances were observed in the solid state $^{13}C$ NMR spectrum of polytetrafluoroxylylene (**P5**) at 133.9 and 127.3 ppm. The lack of a $^{13}C$ NMR peak for the benzylic methylene carbons is not unexpected as the two fluorine substitiuents are not decoupled from the benzylic carbon, therefore dipole-dipole coupling eliminates the resonance for the fluorinated methylenes.[10] Interrupted decoupling strongly attenuated the 127.3 ppm peak (*C*H aromatic) leaving the peak at 134.2 ppm (*C* aromatic) relatively unchanged.

## Conclusions

Polyxylylenes **P1-P5** were successfully characterized using solid state $^{13}C$ CP MAS NMR spectroscopy. The $^{13}C$ NMR chemical shift data, in combination with the results of interrupted decoupling experiments, allowed assignment of resonances to their respective carbon sources in the polymers. These NMR data confirmed the integrity of the xylylene building block in the polymers, and are consistent with linear polymers. No evidence of crosslinking could be detected within the sensitivity limits of the NMR. Residual paracyclophane was detected by $^{13}C$ CP MAS NMR spectroscopy in the polyxylylene samples prepared at room temperature. However, discrete $^{13}C$ resonances due to amorphous and crystalline phases in the polymers were not resolved.

Table. $^{13}C$ NMR and Interrupted Decoupling Chemical Shifts for polyxylylenes.

| **Polymer** | **$^{13}C$ NMR Resonances (ppm)** | | **Interrupted Decoupling (ppm)** | |
|---|---|---|---|---|
| | **Aromatic** | **Aliphatic** | **Aromatic** | **Aliphatic** |
| **P1** | 141.4, 139.7,<br>128.9 | 39.8 | 141.4, 140.2,<br>129.4 | ---- |
| **P2** | 141.4, 139.7,<br>128.9 | 39.8, 24.0, 16.0 | ---- | ---- |
| **P3** | 142.3, 137.4,<br>134.3, 130.5 | 36.9 | 142.3, 137.1,<br>134.8 | ---- |
| **P4** | 139.0, 132.5 | 33.7 | 138.8, 135.0 | ---- |
| **P5** | 133.9, 127.3 | ---- | 134.2 | ---- |

## Acknowledgments

We would like to thank Professor William R. Dolbier, Jr. at the University of Florida for the sample of octafluoroparacyclophane. We would also like to thank David R. Wheeler at Sandia for his valuable comments and discussions. This work was supported by the United States Department of Energy under contract #DE-AC04AL85000.

## References

1. For reviews of polyxylylene and xylylene chemistry see: a) Ereede, L. A.; Swarc, M. *Q. Rev. Chem. Soc.* **1958**, *12*, 301. b) Lee, S. M. Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol 24, John Wiley & Sons, New York, 1983, 744-771. c) Mulvaney, J. E. *Polym. Sci. Technol.* **1984**, 25. d) Beach, W. F.; Lee, C.; Bassett, D. R.; Austin, T. M.; Olson, R. Encyclopedia of Polymer Science and Engineering, 2nd ed., Vol 17, John Wiley & Sons, New York, 1989, 990-1025.
2. Gorham, W. F., U. S. Pat. 3, 342, 754 (Sept 19, 1967).
3. The driving froce for ring opening is the strain energy of the [2.2]paracyclophane which was determined to be 138 kJ/mol. See Hopf, H.; Marquard, C. in *Strain and Is Implications in Organic Chemistry* (A. de Meijere and S. Blechert, Eds.) Kluwer, Dordrecht, 1989, p. 297.
4. Gorham, W. F. *Am. Chem. Soc. Polym. Chem. Preprints* **1965**, *6*, 73.
5 a) Koenig, J. L. Spectroscopy of Polymers, American Chemical Society, Washington, D.C., 1992, Chapters 8-9. b) High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk, R. A. Komoroski, Ed., VCH Publishers, Deerfield Beach, Florida, 1986.
6. Loy, D. A.; Assink, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 3977-78.
7. Dolbier, W. R., Jr.; Asghar, M. A.; Pan, H. Q.; Celewicz, L. *J. Org. Chem.* **1993**, *58*, 1827.

8. $^{13}C$ NMR: δ 139.4 (C aromatic), 132.8 (CH aromatic), and 35.7 (methylene) ppm from Takemura, T.; Sato, T. *Can J. Chem.* **1976**, *54*, 3412.
9. Review: Vogtle, F.; Newmann, P. *Top. Curr. Chem.* **1974**, *48*, 67.
10. Slichter, C. P. Principles of Magnetic Resonance, 3rd ed., Springer-Verlag, Berlin, 1990, p 65.

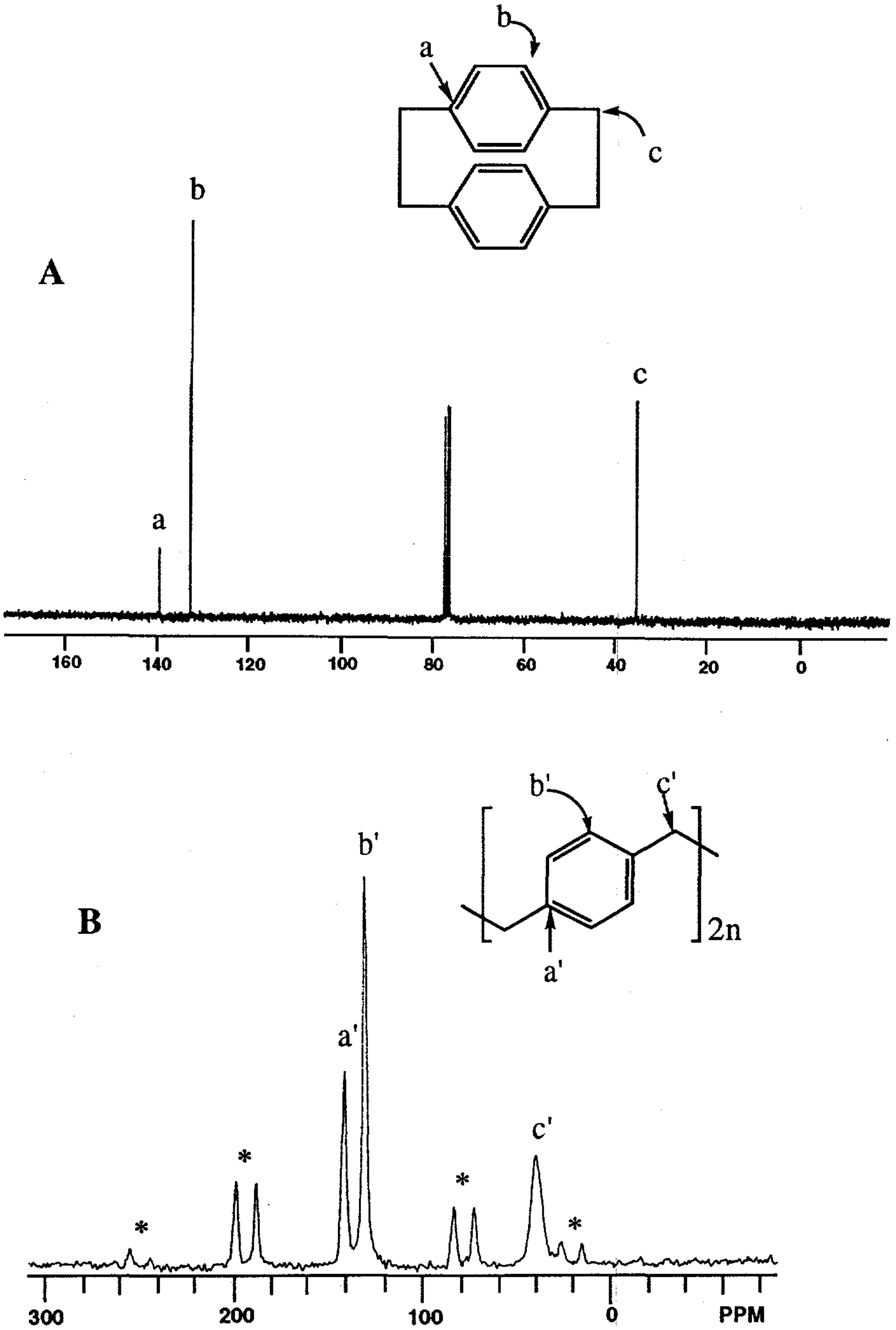


Figure 2. Solution $^{13}C$ NMR spectrum of [2.2]paracyclophane (A) and solid state $^{13}C$ CP MAS NMR spectrum of polyxylylene (B) prepared by pyrolyzing [2.2]paracyclophane at 650 °C. The three peaks at 77.00 ppm in A are due to solvent and the asterisks mark spinning side bands in B.

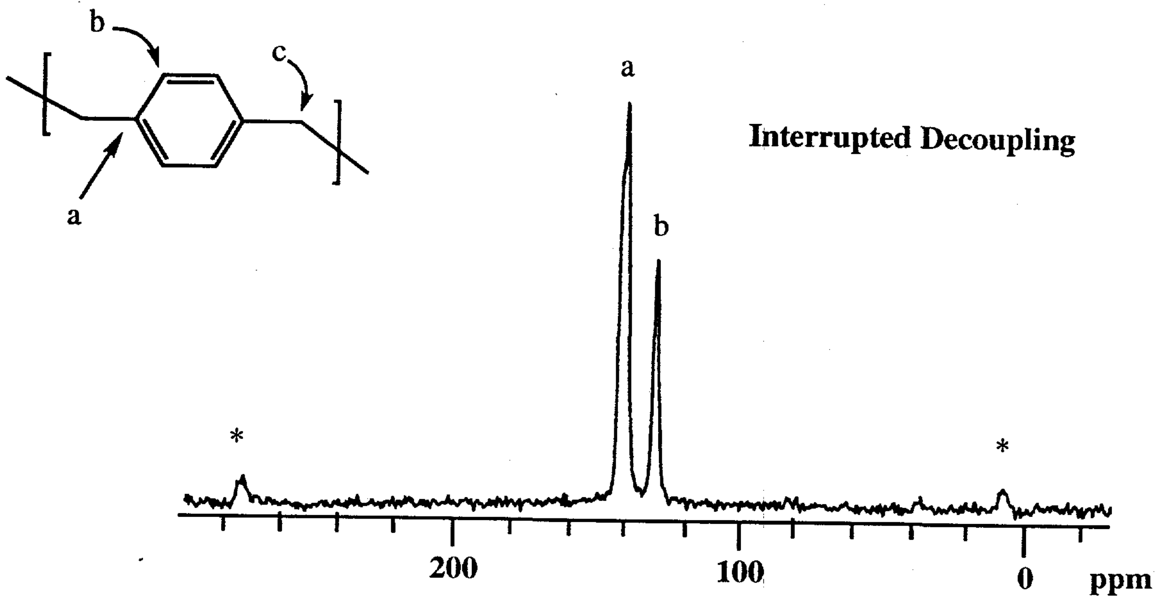


Figure 3. The $^{13}$C CP MAS NMR spectrum of polyxylylene **P1-(-78)** obtained with interrupted decoupling. Peaks due to carbon nuclei with hydrogens attached (b) are attenuated more than those without hydrogens (a). The resonance due to the methylene carbons (c) at 38 ppm has disappeared entirely (the asterisks mark spinning side bands).