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Characterization of Poly(xylylenes) with Solid-State ^{13}C Nuclear Magnetic Resonance Spectroscopy[†]

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ABSTRACT: Poly(xylylenes) are an important class of thermoplastics that are readily prepared by thermolysis of [2.2]paracyclophane or xylene precursors to afford xylylene monomers that condense and polymerize on solid surfaces to give polymer films. As most poly(xylylenes) are insoluble due to a high degree of crystallinity, characterization by solid-state nuclear magnetic resonance spectroscopic techniques is necessary. In this paper we describe the preparation of poly(xylylene) (**P1**), poly(2-ethylxylylene) (**P2**), poly(2-chloroxylylene) (**P3**), poly(2,3-dichloroxylylene) (**P4**), and poly(α,α,α′,α′-tetrafluoroxylylene) (**P5**) and their characterization using solid-state ^{13}C cross polarization magic angle spinning nuclear magnetic resonance (CP MAS NMR) spectroscopy.

Introduction

Poly(xylylenes) 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 furnance where it is thermally cleaved into two equivalents of xylylene monomer.[3] Xylylenes[4] are reactive quinodimethane monomers that polymerize and crystallize simultaneously with condensation on cool surfaces.[5] Polymerization involves the combination of xylylene monomers to form a telechelic diradical that grows with continued additions of xylylene molecules to the ends of the polymer chain. The end result of the Gorham process is a solvent-free film composed of linear, highly crystalline, high molecular weight polymer.[6] Poly(xylylene) and chloro-substituted poly(xylylenes) 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 poly(xylylenes) a valuable class of encapsulants.

These same characteristics also make poly(xylylene) and poly(haloxylylenes) difficult to characterize by analytical techniques, such as solution nuclear magnetic resonance (NMR) spectroscopy. Highly crystalline poly(xylylenes) can be characterized by X-ray diffraction,[1b,d] but the structures of amorphous polymers or polymers with poorly defined crystalline domains are not as easily determined. 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 the molecular structure of both types of materials.[7]

We became interested in structurally characterizing poly(xylylene) materials as part of our study of fullerene–xylylene copolymers.[8] Solid-state ^{13}C CP MAS NMR and interrupted decoupling experiments[7] were used to determine the structures of the copolymers. It was noted during this investigation that ^{13}C NMR spectra had not been previously reported for any of the poly(xylylenes). In this paper we describe the preparation of poly(xylylene) (**P1**), poly(2-ethylxylylene) (**P2**), poly(2-chloroxylylene) (**P3**), poly(dichloroxylylene) (**P4**), and poly(α,α,α′,α′-tetrafluoroxylylene)[9] (**P5**) (Figure 1) by the pyrolysis of their respective [2.2]paracyclophanes and their characterization using solid-state ^{13}C CP MAS NMR spectroscopy. Poly(2-ethylxylylene) (**P2**), a soluble poly(xylylene), was also examined by solution ^{13}C NMR spectroscopy. Introduction of ethyl substituents on the phenylene ring does not interfere with the formation of xylylene monomers or their polymerization, but crystallinity of the polymer is drastically reduced.[10] Apparently, the bulky ethyl substituents interfere with the growth of crystallites, allowing amorphous, soluble poly(ethylxylylenes) to form. Soluble poly(ethylxylylenes) are useful as coatings for substrates where it may be necessary to remove the polymer at a later time, such as for art or book preservation.

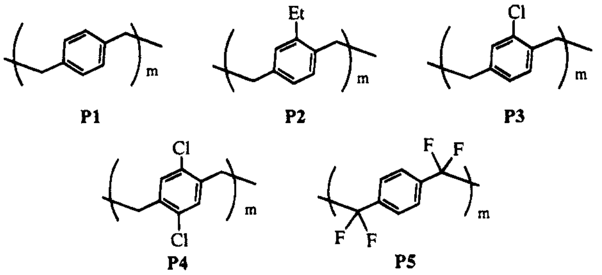
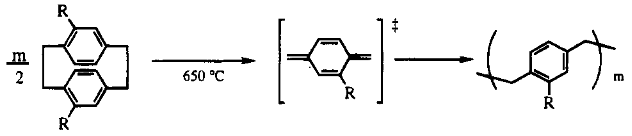


Figure 1. Poly(xylylenes) (**P1**–**P5**) prepared by pyrolysis of [2.2]paracyclophanes and characterized by solid-state ^{13}C NMR spectroscopy.

Scheme 1. Formation and Polymerization of Xylylene Monomers 1–5 from Paracyclophanes



Experimental Section

General Procedures. [2.2]Paracyclophane, dichloro[2.2]paracyclophane, tetrachloro[2.2]paracyclophane, and diethyl-

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[2.2]paracyclophane were obtained from Union Carbide and used as received. α,α,α,α,α′,α′,α′,α′-Octafluoro[2.2]paracyclophane was obtained from Professor William R. Dolbier, Jr., at the University of Florida. *p*-Xylene-α,α′-$^{13}C_2$ (99% isotopically labeled) was obtained from Cambridge Isotopes and used as received. Infrared analyses were performed with thin films in a Perkin-Elmer 1750 Fourier transform infrared spectrometer. Solution ^{13}C NMR spectra of [2.2]paracyclophane precursors were obtained in deuteriochloroform 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 and 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 sidebands 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 mmHg) and the xylylene monomers generated were condensed/polymerized on glass at 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 h at room temperature. Thick films were opaque and generally white, though poly(xylylene) films were occasionally tinted gray-green. Thin films prepared at room temperature were transparent.

Nomenclature. In order to distinguish between monomers **1**−**5** and the resulting polymers, the latter are designated as ***PX***, where **P** refers to polymer and ***X*** is the number of the monomer used in the polymerization. For **P1** there are additional numbers after the hyphen that indicate the surface temperature at which the polymer formed.

Poly(xylylene) P1-25. [2.2]Paracyclophane (2.0 g, 9.6 mmol) was sublimed under reduced pressure into a quartz tube heated to 650 °C over a period of 5 min. A white film of poly(xylylene) **P1-25** was formed at room temperature (0.43 g, 22%). The remainder of the mass in the polymerization is believed to be carbon and polymer in the thermolysis tube (0.14 g, 7%), unreacted material (0.99 g, 50%), and volatile pyrolysis products. IR (KBr) 3045, 3016, 2921, 2855, 1511, 1452, 1415, 1205, 1139, 1082, 1020, 822, 544 cm^{-1}; ^{13}C CP MAS NMR (50.198 MHz) δ 201.2 (ssb), 190.2 (ssb), 141.4 (shoulder), 139.7 (C aromatic), 128.9 (CH aromatic), 79.7 (ssb), 68.5 (ssb), 39.8 (CH_2); ^{13}C interrupted decoupled NMR (50.19 MHz, D_1 = 90 μs) δ 272.8 (ssb), 141.4, 140.2, 129.4, 7.7 (ssb).

Poly(xylylene) P1-0. [2.2]Paracyclophane (2.0 g, 9.6 mmol) was sublimed into a quartz tube heated to 650 °C. Poly(xylylene) **P1-0** was formed in a flask cooled to 0 °C with an ice bath (0.43 g, 22%). ^{13}C CP MAS NMR (50.198 MHz) δ 201.2 (ssb), 190.2 (ssb), 141.4 (shoulder), 140.0 (C aromatic), 129.2 (CH aromatic), 79.7 (ssb), 68.5 (ssb), 40.0 (CH_2).

Poly(xylylene) P1-(−78). [2.2]Paracyclophane (2.0 g, 9.6 mmol) was sublimed into a quartz tube heated to 650 °C. Poly(xylylene) **P1-(−78)** was formed in a flask cooled to −78 °C with a dry ice−acetone bath (0.65 g, 32%). ^{13}C CP MAS NMR (50.198 MHz) δ 253.9 (ssb), 196.6 (ssb), 186.1 (ssb), 139.5 (C aromatic), 128.8 (CH aromatic), 82.3 (ssb), 71.8 (ssb), 39.4 (CH_2), 32.6 (ssb), 14.4 (ssb); ^{13}C interrupted decoupled NMR (50.19 MHz) δ 196.5 (ssb), 139.5, 129.1, 83.7.

^{13}C-Enriched Poly(xylylene) P1′. α,α-^{13}C-enriched *p*-xylene was distilled into a pyrolysis tube heated to 1000 °C. ^{13}C-enriched poly(xylylene) **P1′** was formed at room temperature. ^{13}C CP MAS NMR (50.198 MHz) δ 140.6 (C aromatic), 129.1 (CH aromatic), 37.8 ($^{13}CH_2$), 23.7 (CH_3); ^{13}C interrupted decoupled NMR (50.19 MHz, D_1 = 50 μs) δ 140, 39, 22.

Isolation of [2.2]Paracyclophane from Poly(xylylene). Poly(xylylene) **P1-25** (2.1 g, 81%) was prepared as above from [2.2]paracyclophane (2.57 g, 12.3 mmol) by condensation of the xylylene at room temperature as a thin translucent film. The film (1.40 g) was extracted with benzene in a Soxhlet extractor for 24 h. The benzene was removed *in vacuo* to afford a white solid (0.20 g, 14%). ^{13}C NMR (50.198 MHz, $CDCl_3$) δ 139.6 (C aromatic), 133.0 (CH aromatic), 128.3 (benzene), 35.68 (CH_2).

Poly(2-ethylxylylene) (P2). Diethyl[2.2]paracyclophane (2.0 g, 7.6 mmol) was distilled into a pyrolysis tube at 650 °C, affording poly(ethylxylylene) (0.74 g, 37%). IR (KBr) 3005, 2921, 2855, 1610, 1511, 1453, 1020, 886, 824, 547 cm^{-1}; ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 143.23, 139.73, 139.67, 139.38, 137.25, 134.55, 133.40, 133.24, 133.15, 133.02, 132.10, 132.05, 130.10, 130.04, 128.64, 35.72, 35.41, 35.14, 34.26, 33.35, 26.95, 14.22; ^{13}C CP MAS NMR (50.198 MHz) δ 201.2 (ssb), 190.2 (ssb), 141.4 (shoulder), 139.7 (C aromatic), 128.9 (CH aromatic), 79.7 (ssb), 68.5 (ssb), 39.8 (CH_2), 24.0 (CH_2), 16.0 (CH_3).

Poly(2-chloroxylylene) (P3). Dichloro[2.2]paracyclophane (2.0 g, 7.2 mmol) was sublimed into a quartz tube at 650 °C. A white film was collected (0.4 g, 20% yield). IR (KBr) 3018, 2927, 2861, 1608, 1559, 1494, 1452, 1402, 1209, 1050, 878, 826, 687 cm^{-1}; ^{13}C CP MAS NMR (50.198 MHz) δ 226 (ssb), 222 (ssb), 204 (ssb), 142.3, 137.4, 134.3, 130.5, 69.7 (ssb), 63.5 (ssb), 57.0 (ssb), 36.9 (CH_2); ^{13}C interrupted decoupled NMR (50.19 MHz) δ 142.3, 137.1, 134.8.

Poly(dichloroxylylene) (P4). Tetrachloro[2.2]paracyclophane (2.0 g, 5.8 mmol) was sublimed into a quartz tube heated to 650 °C. A white film was collected (0.58 g, 29% yield). IR (KBr) 2930, 1601, 1550, 1476, 1376, 1122, 1078, 886, 792 cm^{-1}; ^{13}C CP MAS NMR (50.198 MHz) δ 208.4 (ssb), 139.0, 132.5, 70.0 (ssb), 33.7 (CH_2); ^{13}C interrupted decoupled NMR (50.19 MHz) δ 138.8, 135.0.

Poly(tetrafluoroxylylene) (P5). Octafluoroparacyclophane (0.79 g, 2.25 mmol) was sublimed into a quartz tube at 650 °C. A white film was collected (0.41 g, 51.6% yield) at room temperature. IR (KBr) 1415, 1261, 1150, 1093, 1009, 980, 929, 899, 838, 794, 715 cm^{-1}; ^{13}C CP MAS NMR (50.198 MHz) δ 200 (ssb), 133.9, 127.3, 67.0 (ssb); ^{13}C interrupted decoupled NMR (50.19 MHz) δ 134.2.

Results

Thermolysis of paracyclophanes in a flow-through pyrolysis apparatus afforded thin films of poly(xylylenes). [2.2]Paracyclophane and the halogenated paracyclophanes were sublimed into an evacuated quartz tube. The ethyl-substituted dimer melts at 45 °C and was distilled into the apparatus. 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. Poly(xylylene) films that formed when pyrolysates condensed onto surfaces cooled to −78 °C (**P1-(−78)**) were fragile, while those formed at 0 °C (**P1-0**) or room temperature (**P1-25**) were uniform and tough. Yields of the polymers based on monomer ranged between 20 and 50% and were based only on material that condensed on the inner surface of a receiving flask placed in a controlled temperature bath.

Flexible poly(xylylene) 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 poly(xylylenes) **P1**−**P4** are similar to reported spectra.[1c]

Poly(xylylene). 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 poly(xylylenes). The solution ^{13}C NMR spectrum was made up of three signals representing the substituted (139.6 ppm) and unsubstituted (133.0 ppm) aromatic and benzylic methylene (35.7 ppm) carbons.[11] The solid-state ^{13}C CP MAS NMR spectrum of poly(xylylene) **P1-(−78)** (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 poly(xylylenes), indicating that the polymers were not oligomeric.

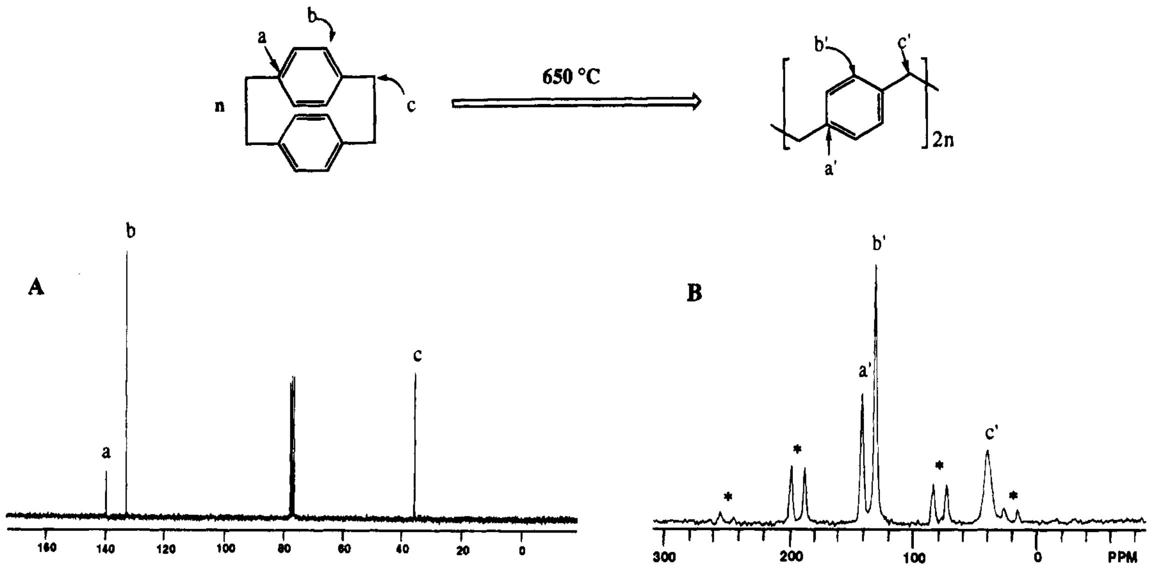


Figure 2. Solution ^{13}C NMR spectrum of [2.2]paracyclophane (A) and solid-state ^{13}C CP MAS NMR spectrum of poly(xylylene) (B) prepared by pyrolyzing [2.2]paracyclophane at 650 °C. The three peaks at 77.00 ppm in A are due to solvent, and the asterisks mark spinning sidebands in B.

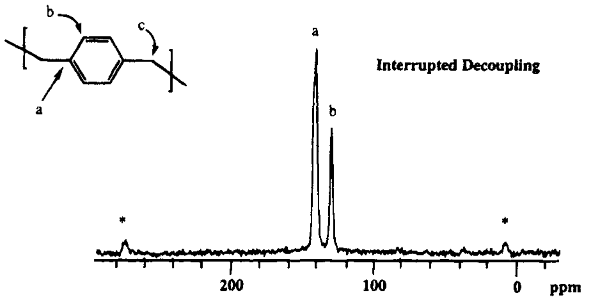


Figure 3. ^{13}C CP MAS NMR spectrum of poly(xylylene) **P1-(−78)** obtained with interrupted decoupling. Peaks due to carbon nuclei with hydrogens attached (b) are attenuated more than those without hydrogens (a). The resonance due to the methylene carbons (c) at 38 ppm has disappeared entirely (the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

Interrupted decoupling experiments with **P1-(−78)** 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 entirely disappeared, 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.

The crystallinity of poly(xylylenes) can be controlled by changing the temperature of the substrate on which the monomer condenses and polymerizes.[1b] Samples of poly(xylylene) prepared at different temperatures (**P1-25**, **P1-0**, and **P1-(−78)**)[12] were examined by ^{13}C CP MAS NMR spectroscopy. Closer examination of the spectrum of the poly(xylylene) prepared at room temperature (**P1-25**) revealed a shoulder on the peak at 139.7 ppm (Figure 4). Interrupted decoupling experiments attenuated the major peak, leaving the shoulder behind. A shoulder on the peak of the benzylic methylene was not observed in any of these experiments but could easily be hidden within the wider peak at 40 ppm. However, in a sample of α,α′-^{13}C-enriched poly(xylylene), a shoulder was clearly visible downfield from the major peak (Figure 5).

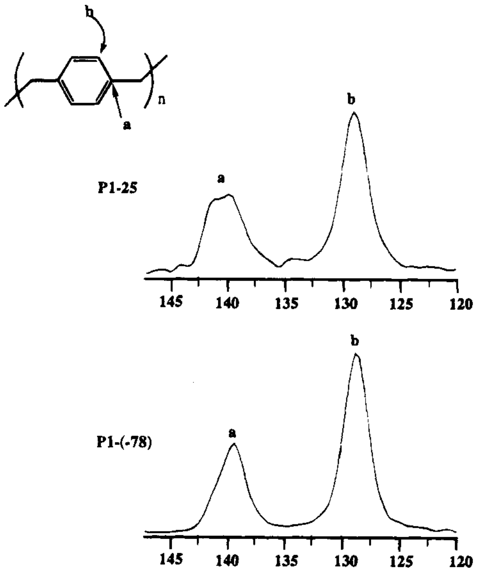


Figure 4. Aromatic regions of the ^{13}C CP MAS NMR spectra of two poly(xylylenes) prepared by condensation of xylylene at room temperature (**P1-25**) and at −78 °C (**P1-(−78)**). The shoulder on the peak at 141.4 ppm in the spectrum of **P1-25** represents [2.2]paracyclophane that was deposited in the poly(xylylene) film during the polymerization process. No shoulder is apparent in **P1-(−78)**.

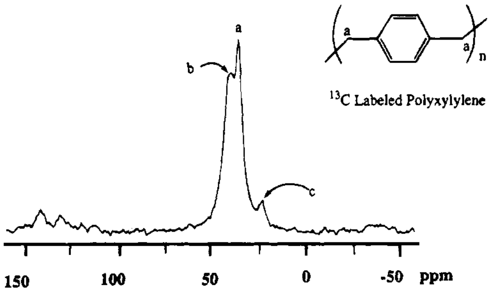
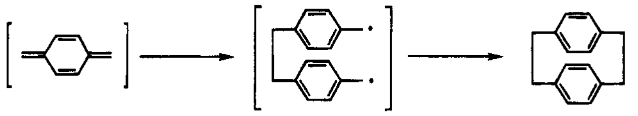


Figure 5. The ^{13}C CP MAS NMR spectrum of the α,α-^{13}C-enriched poly(xylylene) also reveals a shoulder (b) due to [2.2]paracyclophane deposited in the polymer and some terminal methyl groups (c).

Because poly(xylylenes) are known to have both amorphous and crystalline components, it was first

Scheme 2. Dimerization of Xylylene Monomer 1 to Regenerate [2.2]Paracyclophane



thought that the shoulders in the NMR spectra were due to multiple phase(s) within the samples; solid-state ^{13}C NMR has been used to differentiate between crystalline and amorphous polymers based on chemical shifts and differences in spin–lattice relaxation times.[8] Another possible origin for the shoulders in the NMR spectra is the presence of [2.2]paracyclophane in the polymer, deposited during the vapor deposition polymerization process. While the Gorham process is sometimes purported to result in polymers free of paracyclophanes,[1c,2] cyclic dimer and trimer have been detected in poly(xylylene) samples by X-ray diffraction.[13] [2.2]Paracyclophane either can be swept through the pyrolysis tube intact or formed by cyclization of the dimer diradical (Scheme 2).[14]

In order to determine if the shoulders in the solid-state NMR spectra of poly(xylylene) were due to [2.2]paracyclophane, attempts were made to obtain the ^{13}C CP MAS NMR spectrum of the pure dimer as a reference. Interestingly, ^{13}C resonances could not be detected under a wide range of cross polarization conditions, including those used to analyze the poly(xylylenes). This difficulty is probably related to the relative ease with which this molecular solid rotates.[15] When the correlation time for molecular motion is equal to the modulation period of the ^{1}H decoupling field, the C–H dipolar interactions are not effectively averaged. The resonance lines are then broadened to the point of being unobservable, making it impossible to obtain a reference spectrum of the pure [2.2]paracyclophane. However, it is not surprising that the dimer would be observed by solid-state NMR in the polymer matrix since its rotational motion, and thus its C–H dipolar interactions, would be strongly affected by its environment.

Final proof for the presence of [2.2]paracyclophane came from experiments in which the dimer was isolated from samples of poly(xylylene). Soxhlet extraction of poly(xylylene) **P1-25** with benzene recovered considerable [2.2]paracyclophane (14.2% by weight). In addition, when α,α'-^{13}C-enriched poly(xylylene) was washed with benzene and reexamined by ^{13}C CP MAS NMR, the subsequent spectrum of the polymer revealed that the shoulder on the benzylic carbon resonance had disappeared. Therefore, the shoulders in the spectra of poly(xylylenes) prepared at room temperature were due to the cyclic dimer deposited within the polymer rather than the resolution of different crystalline and/or amorphous components.

Poly(2-ethylxylylene). Poly(2-ethylxylylene) (**P2**) was soluble in aromatic and chlorinated organic solvents. Characterization of **P2** by solution ^{13}C NMR and solid-state ^{13}C CP MAS spectroscopies (Figure 6) permitted direct comparison of the spectra obtained by the two techniques. In the solid-state spectrum, there were fewer but broader peaks than observed in the liquid sample. Two aromatic resonances were visible at 138 and 125 ppm, corresponding to two groups of peaks near 139 and 131 ppm in the solution spectrum. Experience with the solid-state NMR study of **P1** has indicated that the peak farther downfield in the aromatic region was due to the substituted carbons, while the peak at 125 ppm arose from the unsubstituted aromatic carbons. Based on the chemical shift assignments for **P1**, the peak at 38 ppm was assigned to the benzylic methylene carbons. The methylene and methyl carbon resonances of the ethyl substituents lay at 24 and 16 ppm, respectively, in the solid-state spectrum and at 26.9 and 14.2 ppm in the solution spectrum.

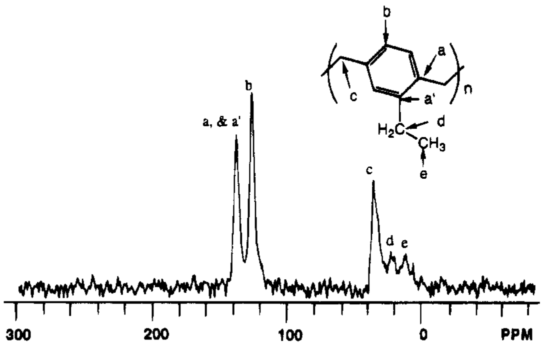


Figure 6. ^{13}C CP MAS NMR spectrum of poly(ethylxylylene) (**P2**) revealing aromatic (a, a', and b) and aliphatic carbons (c, d, and e).

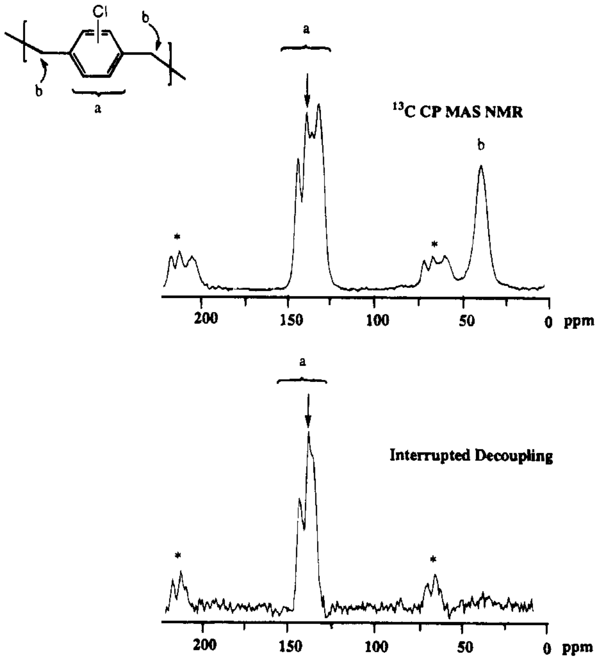


Figure 7. ^{13}C CP MAS NMR spectrum (top) and interrupted decoupling experiment (bottom) for poly(chloroxylylene) (**P3**). The asterisks mark spinning sidebands. The arrows mark 137.3 ppm in the spectra.

Poly(chloroxylylene). Dichloro[2.2]paracyclophanes are prepared by chlorination of [2.2]paracyclophane.[16] As a result, chlorinated paracyclophanes are a mixture of regioisomers. Separation of the isomers is not necessary, however, as a single 2-chloroxylylene monomer is formed upon pyrolysis. The ^{13}C CP MAS NMR spectrum of poly(chloroxylylene) (**P3**) displayed the benzylic methylene resonance at 36.9 ppm. The aromatic region of the spectrum was more complex with a total of four broad resonances at 130.5, 134.3, 137.4, and 142.3 ppm (Figure 7). Interrupted decoupling with a 60 μs delay reduced the number of resonances in the aromatic region to three at 142.3, 137.1, and 134.8 ppm, arising from the three unprotonated carbons in the phenylene group.

Poly(dichloroxylylene). Tetrachloro[2.2]paracyclophane is also prepared as an isomeric mixture by the chlorination of [2.2]paracyclophane. Poly(dichloroxylylene) (**P4**) was also characterized by solid-state ^{13}C CP MAS NMR spectroscopy (Figure 8). In addition to the benzylic methylene resonance at 33.7 ppm, two

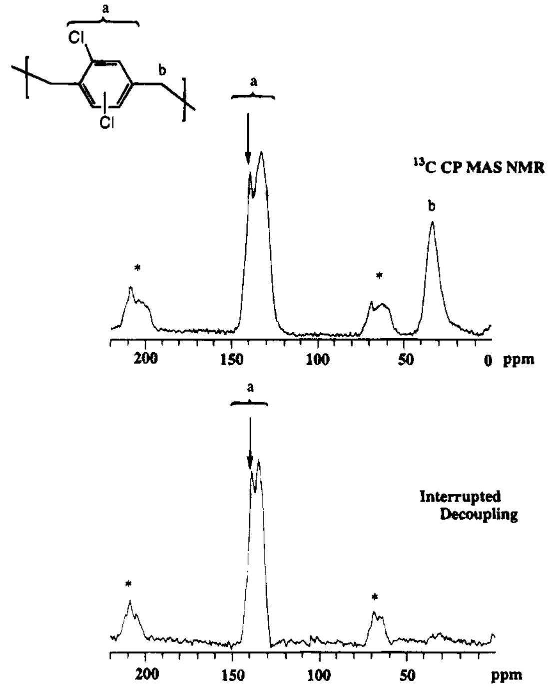


Figure 8. ^{13}C CP MAS NMR spectrum (top) and interrupted decoupling experiment (bottom) for poly(dichloroxylylene) (**P4**). The asterisks mark spinning sidebands. The arrows mark 139 ppm in the spectra.

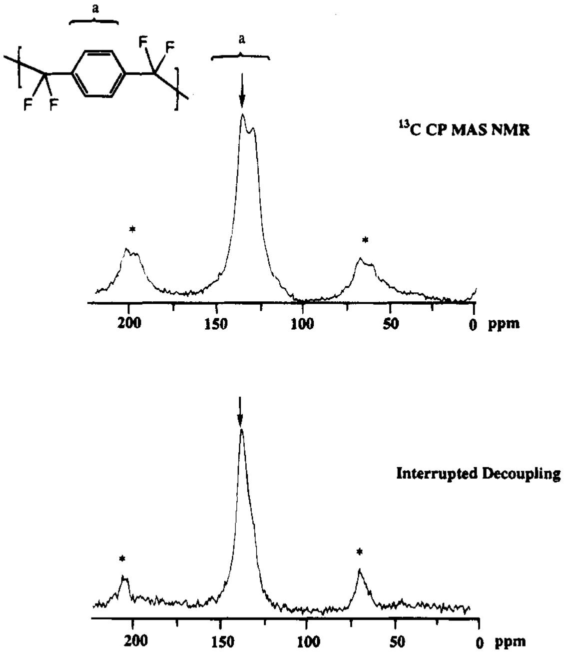


Figure 9. ^{13}C CP MAS NMR spectrum (top) and interrupted decoupling experiment (bottom) for poly(tetrafluoroxylylene) (**P5**). The asterisks mark spinning sidebands. The arrows mark 134 ppm in the spectra.

aromatic resonances at 139.0 and 132.5 ppm were observed. The peak at 132.5 ppm had shoulders on the upfield and downfield sides. Interrupted decoupling left two signals at 138.8 and 135.0 ppm unattenuated.

Poly(tetrafluoroxylylene). Two aromatic carbon resonances were observed in the solid-state ^{13}C NMR spectrum of poly(tetrafluoroxylylene) (**P5**) at 133.9 and 127.3 ppm (Figure 9). The lack of a ^{13}C NMR peak for the benzylic methylene carbons is not unexpected as the two fluorine substituents are not decoupled from the benzylic carbon, therefore dipole–dipole coupling eliminates the resonance for the fluorinated methylenes.[17] Interrupted decoupling strongly attenuated the 127.3 ppm peak (CH aromatic), leaving the peak at 134.2 ppm (C aromatic) relatively unattenuated.

Conclusions

Poly(xylylenes) **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 cross-linking could be detected within the sensitivity limits of the NMR. Residual paracyclophane was detected by ^{13}C CP MAS NMR spectroscopy in the poly(xylylene) samples prepared at room temperature. However, discrete ^{13}C resonances due to amorphous and crystalline phases in the polymers were not resolved.

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References and Notes

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