

Solid-State NMR Study of Na versus K Doping of *para*-Phenylene OligomersMichaël Paris,^{*,†} Laura O. Péres,^{†,‡} Olivier Chauvet,[†] and Gérard Froyer[†]

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¹³C solid-state nuclear magnetic resonance (NMR) experiments were performed on *p*-terphenyl, *p*-quaterphenyl, and *p*-sexiphenyl either in their pristine or doped with alkali metals form. The ¹³C NMR spectra of doped materials show new resonances by comparison with pristine compounds. For the K-doped materials, these resonances appear in the 90–135 ppm range, while for Na-doped materials, they are observed in the larger 20–150 ppm range. It suggests that the interaction between the alkali ions and the oligomers depends on the nature of the alkali. It is corroborated by ¹³C NMR experiments after exposure to air that show different behaviors. As expected, air exposure of K-doped samples restores the pristine spectra. This is not the case for Na doping, where the signature of the doped material persists even after exposure to air. In the latter case, some ¹³C resonances can be assigned to sp³ hybridized carbons and to the quinoid group. It suggests that Na doping induces a polymerization of the oligophenylenes.

Introduction

The use of conjugated polymers has been increasing for the past decade, especially since the discovery of their potential application in polymer-based light-emitting diodes (PLEDs)¹ or in solar cells.² Among them, poly(*p*-phenylene) (PPP) is extensively studied for its potentiality in optoelectronics.³ Its oligomers, like *p*-terphenyl and *p*-quaterphenyl, are already used as UV laser dyes, whereas *p*-sexiphenyl can be useful as an active layer in organic light-emitting devices (OLED).⁴ These oligophenylenes may as well be used as model compounds to understand the chain length effect on the physical properties of PPP. Previous studies were reported so far on electronic and optical properties,⁵ chemical structure⁶ by infrared and UV–visible absorption spectroscopy, Raman scattering, and photoluminescence⁷ or electroluminescence.⁸

The doping process by itself is interesting to study on oligomers of the same series as model compounds because charge stabilization (polarons and bipolarons) is supposed to depend on chain length and alkali metal size. Much work has already been done to understand the doping-induced modifications that result in a transition from the insulating to the conducting state.^{9–12} *n*-Doping can be achieved through a reduction reaction, which is carried out either chemically, in solution, or electrochemically.^{10,12} However intercalation of solvent molecules and nonreproducibility are problems that hinder a straightforward discussion of experimental data.

Solid-state NMR spectroscopy may give a clue to understand the doping process. It was successfully used to explain conformational changes in some conjugated polymers.^{13,14} Both *p*- and *n*-doped polymers, such as polyphenylenevinylene (PPV),^{15,16} polythiophene (PT), polypyrrole (Ppy), or polyaniline (Pan),¹⁷ were also studied by ¹³C solid-state NMR. For doped-PPP, this technique has shown that the counterion mobility depends on

the ion itself, but surprisingly, not upon its size. For example, it seems that Li⁺ ions in Li-doped PPP are less mobile than AsF₆[−] or BP₄[−] anions in *p*-doped PPP.¹⁸ Solid-state NMR spectroscopy also helped a lot in the investigation of alkali-doped C₆₀ materials.^{19,20} We have not found any published report of solid-state NMR studies on doped oligophenylene.

The purpose of this paper is to present and discuss solid-state NMR results obtained on pristine and doped *p*-terphenyl, *p*-quaterphenyl, and *p*-sexiphenyl with two alkali metals (Na and K) of different size in order to further understand the reduction process of these oligomers.

Experimental Section

p-Terphenyl and *p*-quaterphenyl were purchased from commercial sources (Aldrich or Fluka) +99%, and processed without further purification. *p*-Sexiphenyl was prepared as described previously by coupling of 4-bromo-*p*-terphenyl in the presence of nickel complex²¹ (See Figure 1 for general formula).

The doped materials were obtained by intercalation from solution by using Na or K to promote the reduction with liquid ammonia as a solvent. This method results in a solid-state doped material without inserted NH₃, as verified by X-ray photoelectron spectroscopy (XPS).²² The alkali concentration obtained by XPS typically ranges between 0.5 and 1.5 K or Na ion per phenyl ring. It also gives the maximum doping level if we assume that each ion is effectively doping the oligomer. As will be seen, the actual doping level may be much lower. When necessary, the material was also exposed to air for at least 24 h in order to dedope it and to observe the effect of both oxygen or CO₂ contact.

NMR spectra were acquired at room temperature by using a Bruker Avance 500 MHz spectrometer operating at 125.7 and 132.3 MHz for ¹³C and ²³Na, respectively, and by using a 4-mm double-bearing Bruker probehead. MAS (magic-angle spinning) rotor filling of the doped samples was carried out in a dry glovebox under argon, and the rotors were transferred in absence of air. All rotors were spun under dry nitrogen flow. Spectra

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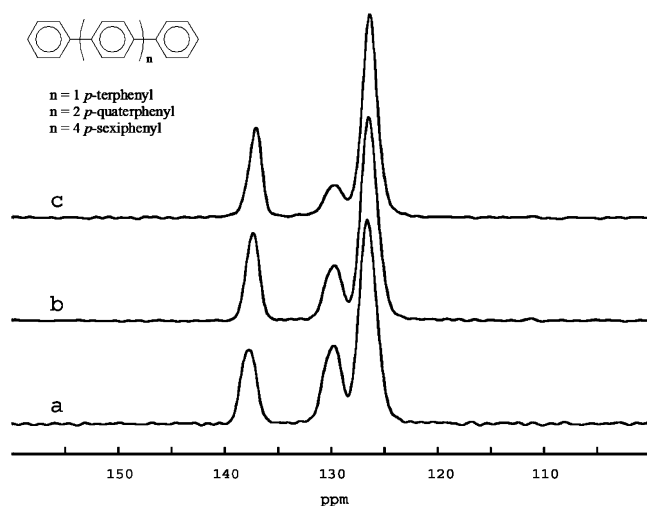


Figure 1. $\{^1\text{H}\}-^{13}\text{C}$ CPMAS (10 kHz) NMR spectra of pristine *p*-terphenyl (a), *p*-quaterphenyl (b), and *p*-sexiphenyl (c). Repetition time was set to 300 s.

were referenced to TMS (tetramethylsilane) for ^{13}C (using adamantane as a secondary reference) and a 1 mol·L $^{-1}$ NaCl solution for ^{23}Na .

$\{^1\text{H}\}-^{13}\text{C}$ RAMP-CPMAS²³ (cross-polarization magic-angle spinning) NMR spectra were acquired by using a 2 ms contact time and a repetition time of 10 or 300 s. ^1H decoupling during acquisition was achieved by using the TPPM method²⁴ with a RF field of approximately 60 kHz. MAS spinning rates were 10 and 8.5 kHz for K and Na related materials, respectively. ^{13}C dipolar dephasing spectra²⁵ were acquired in the same condition as the ^{13}C NMR ones with a dephasing delay of 50 μs . This technique favors quaternary carbons because of the more rapid relaxation of ^1H -bonded carbons due to the stronger $^1\text{H}-^{13}\text{C}$ dipolar coupling during the dephasing delay inserted between excitation of the spins and acquisition of the free induction decay (f.i.d.).

^{23}Na MAS spectrum was acquired by using a rotor-synchronized spin-echo sequence ($\pi/8-\tau-\pi/4-\tau-\text{acq}$) with $\pi/8$ pulse of 6 μs and τ is equal to one rotor period. The pulses were selective, with a radio frequency strength of 10 kHz. Continuous wave ^1H decoupling with a RF field of about 80 kHz was systematically used during acquisition. Repetition time was set to 2 s, and MAS spinning rate to 14 kHz.

Results and Discussion

Pristine Materials. Figure 1 shows the ^{13}C CPMAS spectra of pristine *p*-terphenyl, *p*-quaterphenyl, and *p*-sexiphenyl acquired by using a 300 s repetition time. All the spectra exhibit three resonances at 127, 130, and 137 ppm. From ^{13}C solid-state NMR spectrum of poly(*p*-phenylene)²⁶ and by analogy to the ^{13}C liquid-state spectrum of *p*-terphenyl,²⁷ the 137 ppm line is attributed to quaternary carbons, the 130 ppm line to outer meta carbons, and the 127 ppm line to all remaining carbons. This attribution is further supported by the decrease of the relative intensity of the 130 ppm line from *p*-terphenyl to *p*-sexiphenyl.

Doped Materials. Figure 2b shows the ^{13}C CPMAS spectra of a K-doped *p*-terphenyl sample acquired with a repetition time of 300 s. The spectrum of pristine *p*-terphenyl is shown for comparison in Figure 2a. The fact that the lines at 127, 130, and 137 ppm of the pristine materials are still observed in the K-doped material spectrum shows that both the pristine and doped phases coexist in the samples (doping is nonhomoge-

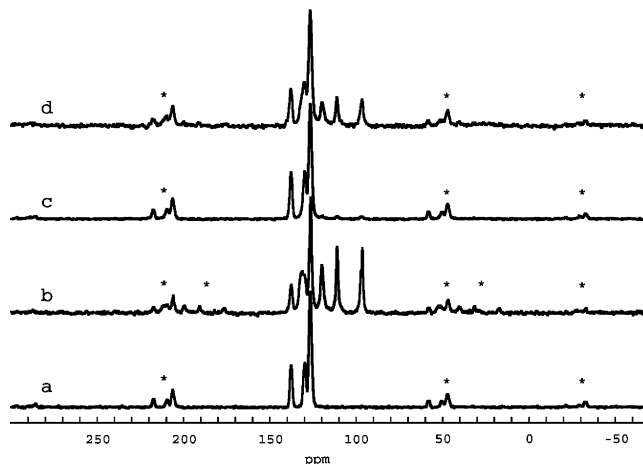


Figure 2. $\{^1\text{H}\}-^{13}\text{C}$ CPMAS (10 kHz) NMR spectra of pristine *p*-terphenyl (a), K-doped *p*-terphenyl sample 1 (b), K-doped *p*-terphenyl sample 2 (c–d). (a–c: repetition time of 300 s; d: repetition time of 10 s). Asterisks denote spinning sidebands.

neous), in agreement with Raman spectroscopy²² and X-ray diffraction data (data not shown). Still, K doping results in the appearance of at least four new lines at 96, 112, 119, and 132 ppm. The average doping levels can be evaluated by comparing the intensities of these new lines obtained with a recycle time of 300 s, with the intensities of the lines corresponding to the pristine materials spectra. We found a proportion of up to 40% for the set of K-doped *p*-terphenyl samples synthesized. We note that these levels are difficult to reproduce experimentally. This is shown in Figure 2c, where the spectrum of a second sample is shown. While the alkali content as determined by XPS is similar (1.2 and 1.0 K ion per phenyl ring), the ^{13}C spectra are quite different. It definitively shows that the alkali concentration does not give the actual doping level and that K must be encountered in chemical species other than intercalants in our samples. Thus, we do not discuss further doping levels by themselves, but we focus our attention on the doping processes.

The spectrum of Figure 2c may be difficult to exploit due to the very weak intensities of the lines associated to the doped materials. Fortunately, doped samples need shorter repetition time than pristine materials. Thus, acquisition of the signal with a small repetition time allows the emphasis of the signal of doped materials by saturating the pristine one. This can be easily observed by comparing the spectra of the same K-doped *p*-terphenyl sample acquired with a repetition time of 300 s (Figure 2c), with the one acquired with a repetition time of 10 s (Figure 2d). Thus, from now, we only consider 10 s repetition time in the following discussion on oligomer samples.

The spectrum of K-doped *p*-quaterphenyl (Figure 3c) exhibits a lot of new lines. At least 9 lines at 135, 131, 123, 119, 117, 115, 108, 105, and 99 ppm can be observed in addition to the pristine ones. Because the 131 and the 123 lines are quite wide and the 119, 117, and 115 ppm lines strongly overlap, hidden lines may still exist. The origin of this multiplicity of lines comparing to the K-doped *p*-terphenyl case is not clear, but this could arise from the complexity of the structure compared to the terphenyl case or from the coexistence of different phases of the K-doped *p*-quaterphenyl in the sample as suggested by X-ray diffraction (data not shown). For the set of K-doped *p*-quaterphenyl samples synthesized, we did not find average doping levels higher than 5%. The spectrum of K-doped *p*-sexiphenyl (Figure 3d) exhibits a unique broad and featureless line centered at 122 ppm and covering the 90–145 ppm range.

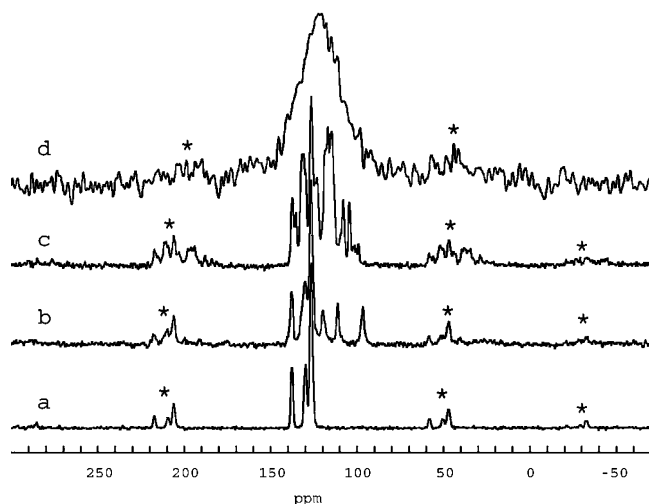


Figure 3. $\{^1\text{H}\}-^{13}\text{C}$ CPMAS (10 kHz) NMR spectra of pristine *p*-terphenyl (a) and K-doped *p*-terphenyl (b), *p*-quaterphenyl (c), and *p*-sexiphenyl (d). Repetition time was set to 10 s for doped materials. Asterisks denote spinning sidebands.

We cannot explain so far why the K-doped *p*-sexiphenyl spectrum is so different from the two others because Raman scattering spectra do not exhibit such a difference.²² The broadening of the ^{13}C NMR spectrum could arise from unpaired electrons not existing in K-doped *p*-quaterphenyl or *p*-terphenyl samples. Because no signal arising from pristine materials can be seen under the broad signal, we were not able to evaluate average doping levels.

The ^{13}C chemical shifts have been related to the local π -electron density in aromatic molecules.^{28,29} In these works, the authors show that the more the line is shifted to low frequency, the lower the π -electron density. Nevertheless, such a relationship is not always straightforward. Indeed, *p*-doped (AsF_5 , I_3) and *n*-doped (K, Na) polyacetylene have shown shifts of the ^{13}C resonances to higher and lower frequencies, respectively.^{30,31} For the three doped oligomers, the new ^{13}C resonances induced by doping appear at a lower frequency than the pristine lines ones (Figure 3), as in the case of *n*-doped polyacetylene.

NMR dipolar dephasing experiments allow assignment of the 96 and 105 ppm lines for K-doped *p*-terphenyl and *p*-quaterphenyl, respectively, to quaternary carbons. This suggests that, for these two materials, the charge-transfer mechanism is similar even if structural differences exist. What happens in K-doped *p*-sexiphenyl is not clear. Nevertheless, both chemical shift range and behavior to air exposure (see below) are similar to the *p*-terphenyl and *p*-quaterphenyl ones and totally different from the Na-doping case exposed hereunder.

A similar behavior is expected for Na doping. Na-doped *p*-terphenyl, *p*-quaterphenyl, and *p*-sexiphenyl spectra are shown in Figure 4. By comparison to K doping, important differences can be observed. Upon Na doping, new lines appear in the 20–50 ppm range, i.e., quite far from the 90–145 ppm range observed in the case of K doping. For Na-doped *p*-terphenyl, five lines are observed at 45, 39, 32, 29, and 27 ppm. For Na-doped *p*-quaterphenyl, four lines appear at 45, 37, 35, and 27 ppm. Finally, the Na-doped *p*-sexiphenyl also exhibits a line at 27 ppm and an unresolved component covering the 30–45 ppm range. Moreover, three, two, and one lines appear also at 148, 144, and 141 ppm for *p*-terphenyl, 148 and 145 ppm for *p*-quaterphenyl, and 145 ppm for *p*-sexiphenyl, respectively. These lines are attributed to quaternary carbons by dipolar dephasing experiments. This range of chemical shifts is generally

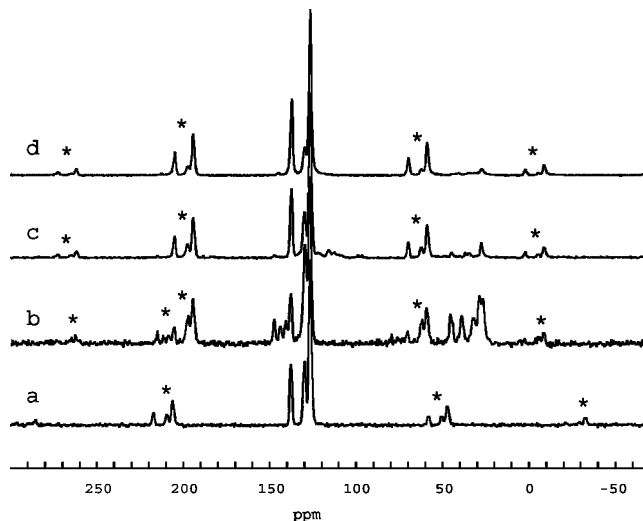


Figure 4. $\{^1\text{H}\}-^{13}\text{C}$ CPMAS NMR spectra of pristine *p*-terphenyl (a) (MAS frequency of 10 kHz) and Na-doped *p*-terphenyl (b), *p*-quaterphenyl (c), and *p*-sexiphenyl (d) (MAS frequency of 8.5 kHz). Repetition time was set to 10 s for doped materials. Asterisks denote spinning sidebands.

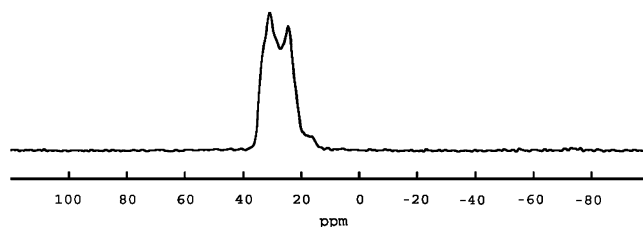


Figure 5. ^{23}Na MAS (14 kHz) NMR spectrum of Na-doped *p*-terphenyl.

assigned to quinoid groups, which have been also observed in these samples by Raman spectroscopy²² or in chemically reduced *p*-sexiphenyl by radical anions such as biphenyl and naphthylsodium or potassium in tetrahydrofuran.³² This fact will be discussed later. As for K doping, Na-doped materials are nonhomogeneous because the lines associated with the pristine materials are still observed in the spectra of the three doped oligomers. The average doping levels are low, about 8% for *p*-terphenyl and 4% for both *p*-quaterphenyl and *p*-sexiphenyl. Thus, considering the Na content determined by XPS, Na must be encountered in chemical species other than intercalant as for the K-doping case. It should be noted that small signals are also observed in the 90–120 ppm range in the Na-doped quaterphenyl spectrum (Figure 4c), suggesting, for this particular sample, a charge-transfer mechanism close to the one observed in K-doped material.

To characterize the samples more deeply, we have performed ^{23}Na NMR experiments. Figure 5 shows the ^{23}Na central transition MAS spectrum of the Na-doped *p*-terphenyl sample. Even by using single-pulse excitation in static sample conditions, there is no evidence of metallic Na or Na counterion signals, presumably because the lines are too broad to be observed. The homogeneous broadening due to unpaired electrons is expected to be more important on ^{23}Na than on ^{13}C nuclei. Indeed, for ^{13}C nuclei, extra spin density is expected to be carried by π orbitals having only a small density of probability on the concerned nucleus. This is not the case for ^{23}Na nuclei, where the extra spin density is carried by an s-type orbital. The unique signal observed in the spectrum exhibits a characteristic second-order quadrupolar line shape under MAS condition with isotropic chemical shift (δ_{iso}) of 36 ppm, a quadrupolar coupling

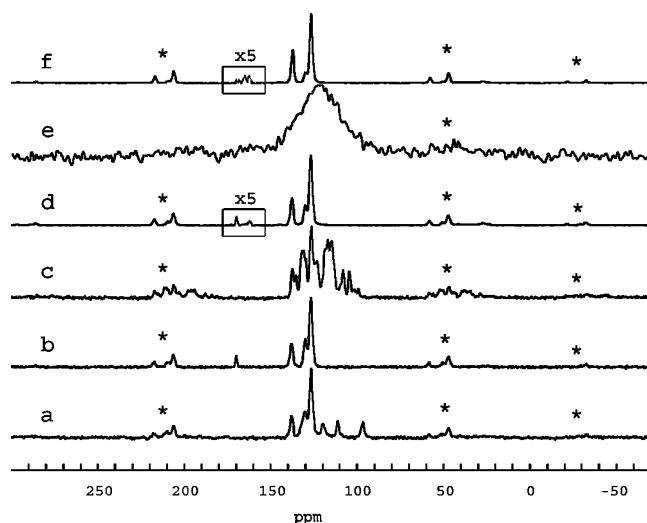


Figure 6. $\{^1\text{H}\}-^{13}\text{C}$ CPMAS (10 kHz) NMR spectra of K-doped *p*-terphenyl (a), K-doped *p*-terphenyl exposed to air (b), K-doped *p*-quaterphenyl (c), K-doped *p*-quaterphenyl exposed to air (d), K-doped *p*-sexiphenyl (e), and K-doped *p*-sexiphenyl exposed to air (f). Repetition time was set to 10 s. Asterisks denote spinning sidebands.

constant (Q_{cc}) of 2.4 MHz, and an asymmetry parameter (η) of 0.3.³³ By comparison to published data,³⁴ this signal is thus attributed to a small amount of NaNH_2 . Obviously, this phase is an impurity phase coming from our synthesis conditions, which may at least partly explain the differences observed between the alkali concentrations and the doping levels. X-ray diffraction patterns have confirmed the presence of NaNH_2 as well of KNH_2 in K-doped samples.

Doped Materials Exposed to Air. In these kinds of compounds, the doping mechanism comes from the intercalation of the alkali ions into the host structure stabilized by a charge transfer. The chemical shift range of the new lines of the K-doped samples gives evidence for a charge-transfer doping. However, in the case of Na doping, the shift is so important that a simple charge transfer is questionable. We have thus decided to expose our doped sample to air and, thus, try to recover the original spectrum because this treatment is known to destroy the charge-transfer doping by formation of alkali oxides or hydroxides.

Figure 6 shows the ^{13}C CPMAS spectra of K-doped *p*-terphenyl (a and b), *p*-quaterphenyl (c and d), and *p*-sexiphenyl (e and f) before and after exposure to air for at least 24 h. In the spectra of the material exposed to air, the lines of the doped material disappear and the resulting spectra look like the pristine ones (Figure 1). It shows that the oligo-*p*-phenylenes are not doped anymore as expected. However, new lines of small intensities appear in the spectra of air-exposed *p*-terphenyl (170 ppm), *p*-quaterphenyl (170 and 162 ppm), and *p*-sexiphenyl (170, 168, 165, and 162 ppm). Their chemical shift range³⁵ indicates that they can be attributed to KHCO_3 (at about 163 ppm) or K_2CO_3 (at about 170 ppm) carbonates formed by contact with CO_2 . It is important to note that the final material is not the same as the starting one because there are new K compounds inside the sample. Actually, the dedoping process is not associated with a deintercalation of the K counterions, but rather to a competitive reaction of the K counterions with air molecules in order to form carbonates and thus disabling the charge transfer.

The situation is quite different in the case of Na doping. As shown in Figure 7b, d, and f for the three Na-doped phenylene oligomers, respectively, the new lines that were formed after

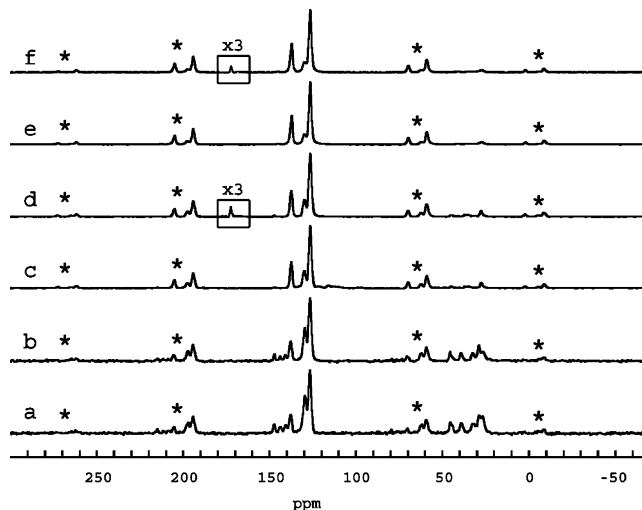


Figure 7. $\{^1\text{H}\}-^{13}\text{C}$ CPMAS (8.5 kHz) NMR spectra of Na-doped *p*-terphenyl (a), Na-doped *p*-terphenyl exposed to air (b), Na-doped *p*-quaterphenyl (c), Na-doped *p*-quaterphenyl exposed to air (d), Na-doped *p*-sexiphenyl (e), and Na-doped *p*-sexiphenyl exposed to air (f). Repetition time was set to 10 s. Asterisks denote spinning sidebands.

the doping process in the 20–50 ppm and 140–150 ppm ranges can still be seen after exposure to air. Actually, the spectra obtained before or after exposure to air are quite similar. Still, the disappearance of the lines in the 95–120 ppm range for Na-doped *p*-quaterphenyl (Figure 7d) after exposure to air is important. As noticed before, it supports the idea that these lines in this specific sample have the same origin as in case of K doping, i.e., they are related to a charge transfer. Conversely, it suggests that the lines observed in the 20–50 ppm and 140–150 ppm range correspond to the formation of a new compound that is stable to air. One can also note the presence of a new line at 172 ppm. It can be attributed to Na_2CO_3 , which is formed by exposure to air.

The survival of the 20–50 ppm and the 140–150 ppm lines suggests that new air-stable compounds have been formed during the Na-doping process. We find it interesting to recall that C_{60} molecules were shown to be able to form covalently bonded polymers upon doping, as reviewed by Forró and Mihály.³⁶ Well-known examples are the AC_{60} and $\text{Na}_2\text{AC}_{60}$ ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$) families, while conventional intercalation compounds (not stable in air) are formed for the other stoichiometries. In these compounds, fullerenes are distorted and two single covalent C–C bonds are formed between adjacent C_{60} . This process is assisted by the charge transfer occurring during doping. It has been evidenced by ^{13}C NMR spectroscopy, which shows sp^3 electronic configurations and nine unequivalent carbon sites^{37–39} due to the C_{60} distortion. It turns out that these materials are stable in air.

In our Na-doped materials, the ^{13}C resonances observed between 20 and 50 ppm are in the chemical shift range of sp^3 hybridized carbons (0–80 ppm). Nevertheless, one can also imagine sp^2 carbon resonances shifted by hyperfine coupling, but in this case, the great chemical shift anisotropy (CSA) of sp^2 carbons should give rise to spinning sidebands, which are not observed in the spectra as expected with the small CSA of sp^3 carbons. Thus, in Na-doped samples, the existence of both quinoid groups and sp^3 carbons as well as the air stability allow us to propose, by comparison to the fullerene case, the structure shown in Figure 8, where oligomers polymerize through the formation of a C–C single bond between end-chain carbons.

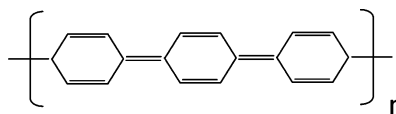


Figure 8. Schematic representation of the proposed air-stable material formed during the Na-doping of *p*-terphenyl.

Nevertheless, further work is needed to clarify the multiplicity of the ^{13}C lines related to intra- and/or intermolecular structures and defects.

Conclusion

The insertion of the alkali metal (K and Na) in the oligo-*p*-phenylene promotes modifications in the ^{13}C NMR spectra. Unfortunately, our synthesis route does not allow the formation of a single-phase material, and doped phases, pristine phases, and impurity phases coexist in the samples. Still, some conclusions can be drawn. In the ^{13}C NMR spectra, resonance shifts to lower frequencies are observed, indicative of a reduction process. Our results show that the doping process is different according to the metal nature. The K-doped materials exhibit an usual doping process. In the case of Na-doped materials, the presence of ^{13}C resonances of quaternary carbons in the 140–150 ppm range suggests the formation of quinoid groups, and resonances in the 20–50 ppm range, the existence of sp^3 hybridized carbons. This difference in the doping process is supported by the air sensitivity of both materials. Indeed, the ^{13}C NMR spectra of air-exposed K-doped materials look like the pristine spectra, whereas they do not change upon exposure to air in the case of Na doping. By analogy with alkali-doped C_{60} , it can be thought of as a polymerization process of the oligo-*p*-phenylenes upon Na doping. Further work is required to isolate the different phases.

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