Communications to the Editor

Application of Solid-State ^{31}P NMR to the Study of Langmuir−Blodgett Films

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Although NMR is a very powerful spectroscopic tool, it has rarely been used to study the molecular structure and organization of Langmuir−Blodgett (LB) films. This lack of use results predominantly from two factors. First, LB films are typically transferred onto flat surfaces of low surface area where the number of nuclei per monolayer (ca. $10^{15}/cm^2$) is well below the conventional NMR detection limit. Second, even when multilayer samples are prepared ($\sim 10^{18}$ molecules/sample), the polymeric substrates onto which the LB films are typically transferred for magnetic resonance studies[1] introduce large ^{1}H and ^{13}C background signals that obscure the interpretation of the NMR spectra[2] of these spin species. However, there are many phosphorus-containing molecules, such as phospholipids and organophosphonic acids, that are of interest as LB films,[3] and here it is demonstrated that ^{31}P magic angle spinning (MAS) NMR can be used to study octadecylphosphonate multilayer LB films. Results show that both quantitative and qualitative information about the film structure can be obtained, and to our knowledge, this is the first NMR study to characterize the structure of an LB film.

Octadecylphosphonic acid (ODPA, $C_{18}H_{37}PO(OH)_2$) is known to form quality Langmuir monolayers and LB films.[4,5] Figure 1a shows the ^{31}P MAS NMR spectrum[6] of a 125-bilayer ODPA LB film[7] with two resolved signals, one at $\delta_{iso} = 28.3$ ppm and the other at $\delta_{iso} = 22.5$ ppm. The signal at 28.3 ppm integrates to approximately 65% of the film structure and can be assigned to the free acid form of ODPA. The isotropic shift of the second signal occurs at $\delta_{iso} = 22.5$ ppm and corresponds to dibasic octadecylphosphonic acid weakly interacting with Cd^{2+} ions which are incorporated into the film for charge stabilization. It is well-known that many LB films are stabilized by the presence of divalent metal ions incorporated into the films,[8] and here a 0.5 mM Cd^{2+} subphase of pH 2.5−3.0 was used. The stronger signal at 28.3 ppm is slightly shifted from $\delta_{iso} = 31.5$ ppm[9] of solid
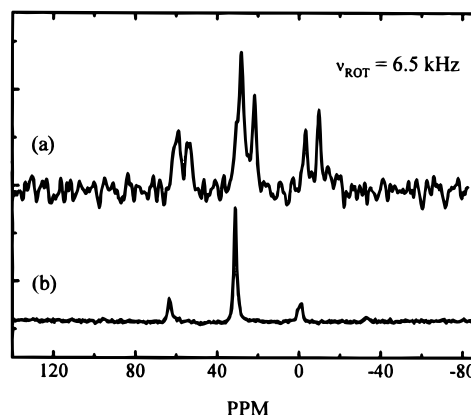
Figure 1. ^{31}P MAS NMR spectra of (a) a 125-bilayer ODPA LB film containing Cd^{2+} ions and of (b) solid octadecylphosphonic acid.

ODPA (Figure 1b) due to weak associations between the free phosphonic acid and nearby Cd^{2+} ions. The assignments for both of these signals are based upon comparison to sodium octadecylphosphonates, where for the mono- and disodium salts, the corresponding ^{31}P NMR resonances are shifted upfield from the free acid form of ODPA and occur a 26.5 and 23.8 ppm, respectively.[10]

Previous work[11,12] on metal phosphonate LB films shows that when films of ODPA are deposited from a 0.5 mM La^{3+} subphase at pH 2.5−3.0, the metal ions are not incorporated in an ion-pairing manner but rather the film crystallizes to form a known solid-state metal phosphonate lattice structure.[13,14] Metal phosphonates form a class of layered mixed organic/inorganic materials that contain two-dimensional continuous inorganic lattice networks that are separated by layers of the organophosphonate substituents.[13−17] LB techniques can be used to prepare single layers of these solid-state materials,[11,12,18,19] and multilayer films can be constructed where one layer of the metal phosphonate is formed during each deposition cycle (Figure 2).

Figure 3 shows ^{31}P MAS NMR spectra of a 35-bilayer and a 125-bilayer lanthanum octadecylphosphonate (ODP) LB film.[20] Note that in the spectra of both samples, only one NMR signal is detected at $\delta_{iso} = 24.8$ ppm. The presence of only one relatively narrow signal reflects a single structure type within the multilayer sample. Previously, others have used ^{31}P MAS NMR to study

(1) Although LB films can be transferred onto other substrates that do not contain C or H atoms (such as Si wafers), Mylar has been the substrate of choice for NMR studies because of the ease with which it can be cut and efficiently packed into NMR rotors.

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(6) MAS NMR spectra were acquired at 11.74 T using a Varian 500 MHz Unity spectrometer equipped with a Jakobsen-type double resonance MAS probe with ^{1}H decoupling. All spectra are referenced to 85% phosphoric acid. MAS spectra were obtained with a recycle delay of 30 s. For the NMR spectra of LB films, a total of 5000 transients were signal-averaged, whereas 32 transients were accumulated to obtain the spectra of the solids.

(7) This film was prepared by transferring ODPA onto a Mylar substrate of dimensions 50 mm × 35 mm × 0.3 mm. All transfer ratios were within the range 0.95−1.03. The sample was cut into thin strips, stacked, and placed vertically into a 5 mm o.d. silicon nitride rotor.

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(20) Both La ODP LB films were prepared as described in an earlier report.[12] Transfer ratios ranged from 0.97 to 1.02. The area of the sample was the same as that of the ODPA LB film.[7]
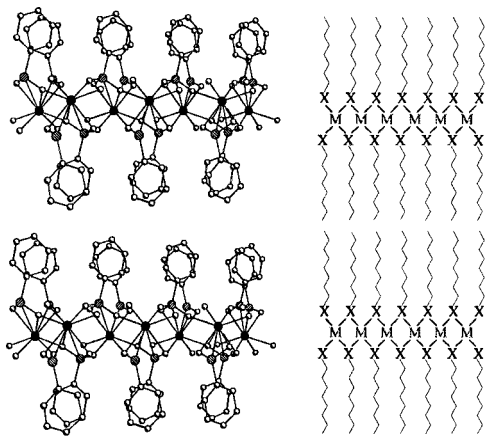
Figure 2. Comparison of the organic/inorganic layered structures of solid-state metal phosphonates to metal phosphonate LB films. (Left) The layered metal phosphonate structure of $LaH(O_3PC_6H_5)_2$. The crystallographic data are taken from ref 13. Key: oxygen and carbon, open circles; phosphorus, hatched circles; and lanthanum, black circles. (Right) Schematic of a metal phosphonate LB film where the polar region contains a 2D inorganic continuous lattice.
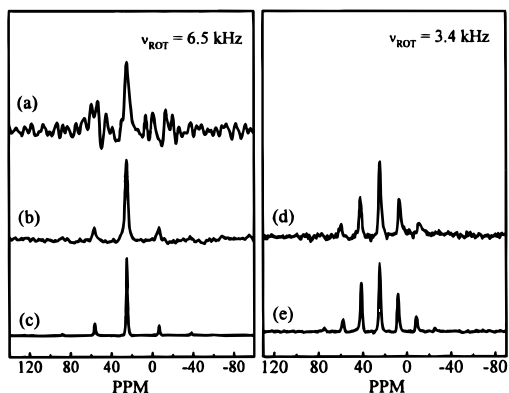
Figure 3. (Left) ^{31}P MAS NMR spectra of (a) a 35-bliayer La ODP LB film, (b) a 125-bilayer La ODP LB film, and of (c) lanthanum butylphosphonate powder each acquired at a spinning rate of 6.8 kHz. (Right) ^{31}P MAS NMR spectra of (d) the same 125-bilayer La ODP LB film and of (e) lanthanum butylphosphonate acquired at a spinning rate of 3.4 kHz.

the metal−oxygen−phosphorus bonding motif in polycrystalline metal phosphonate solids[21−24] and in organophosphonic acids adsorbed onto high surface area particles.[9,10,25] From these earlier

reports it is known that the isotropic shift and the chemical shift anisotropy can be related to the type of metal phosphonate bonding geometry. As is evident from Figure 3, this isotropic shift occurs at the same value as the shift obtained from a sample of polycrystalline lanthanum butylphosphonate and indicates that the structure in the LB film is analogous to that of the powdered solid. In addition, the slower spinning spectrum of the 125-bilayer film displays a well-defined spinning sideband pattern analogous to that of the solid-state polycrystalline material.[26] There are no peaks in the spectrum corresponding to free acid sites in these multilayer assemblies.[27]

These results demonstrate that it is possible to obtain quality ^{31}P MAS NMR spectra of multilayer LB films. In addition, by comparing the spectra of the films with the analogous solid-state materials, a definitive structure of the LB film can be determined. This method takes advantage of the relatively high NMR sensitivity of phosphorus-31 and the lack of any background signals from the substrate that might complicate the interpretation of the spectra. On the basis of the cross-sectional area of the organophosphonates in the $LaH(O_3PR)_2$ structure of 24 $Å^2$/molecule, it is estimated that the 35-bilayer and both 125-bilayer samples contain about 1.0×10^{18} and 3.5×10^{18} ^{31}P nuclei, respectively. Given the signal-to-noise ratio (SNR) of the spectra in Figure 3a and b, a lower detection limit (i.e., SNR of 2:1) of 2.0×10^{17} spins (or 5 bilayers) can be established under the present conditions.[28] This detection limit could be further reduced[29] by obtaining the spectra at higher field, because the signal-to-noise ratio is proportional to $B_0^{11/4}$. Given these factors, a conservative estimate is that ^{31}P MAS NMR with SNR of 8:1 of LB films containing 5 bilayers is possible (assuming a 800 MHz spectrometer). Hence, this technique may find future applications as a general tool for the structural characterization of low surface area thin films containing phosphorus, such as other phosphonate or phospholipid LB films as well as some spontaneously adsorbed multilayer films.[30]

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(26) Slight differences in the intensities of the spinning sidebands of the solid and film are apparent and result from the partial orientation of the LB sample. A detailed fitting of a spinning sideband pattern of a partially oriented system is beyond the scope of this paper and is the focus of future work.

(27) Because the SNR in the spectrum of the 125-bilayer La ODP LB film is 33:1, we can say that the film contains no more than 3% of uncoordinated phosphonic acid sites.

(28) These conditions are dependent upon the packing efficiency of the 5 mm o.d. rotor.

(29) ^1H and ^{31}P cross polarization experiments that used conditions optimized for the analogous solid-state materials did not enhance the signal intensity of the LB films, presumably due to limited mobility of the alkyl chains within the films.

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