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Solid-State Deuterium NMR Studies of Poly(*p*-phenylene) and *trans*-Polyacetylene as a Blend in Polystyrene

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ABSTRACT: Any meaningful model of conductivity in polymers must take into account the nonideal structure and the dynamic heterogeneity of the parent materials. Being largely intractable substances, these polymers do not readily lend themselves to conventional analytical analyses. This paper reports solid-state deuterium NMR results for undoped poly(*p*-phenylene) and for undoped *trans*-polyacetylene as a 13% blend in polystyrene. Methods are presented for (1) determining the crystalline fraction and (2) measuring the motional heterogeneity in these materials. We show that in poly(*p*-phenylene) the predominant mode of motions in the amorphous regions is flips of the phenyl rings by 180°. Relaxation experiments show that these ring flips have a correlation time, τ_c, of approximately 10^{-7} s at ambient temperature. In contrast to the well-defined motions of the phenyl rings in poly(*p*-phenylene), the molecular motions in the amorphous regions of polyacetylene are far more complex and are similar to those observed in the amorphous regions of polyethylene. Furthermore, the blend of polyacetylene in polystyrene is similar to conventional polyacetylene with respect to molecular motion, indicating that domain structures are present in the blend.

Perhaps no other contemporary topic of polymer science has engendered the amount of interest and controversy as have the conducting polymers.[1-3] Driven by a wide range of potential applications, including synthetic metals, battery technology, and solar cell technology,[4-7] this field of endeavor remains at the forefront of polymer research. Polyacetylene and its derivatized, substituted, grafted, and modified analogues have remained the center of research activities directed at synthesizing polymers that conduct electricity and are in addition stable, processable, and mechanically useful. However, other conjugated and/or aromatic polymers have been investigated,[8,9] most notably poly(*p*-phenylene)[10] and poly(phenylene sulfide),[11,12] the latter being particularly attractive because of its commercial availability.

Any meaningful model of conductivity in polymers must take into account the nonideal structure and dynamic heterogeneity inherent in these materials. For example, some workers find that conductivity is related to the architecture and channels in the solid lattice and not so much to the structure of the individual molecules.[13] Others, in contrast, conclude that conductivity arises mainly from transport of charge along the individual chains.[14-16] Both approaches apparently apply.

Complete chemical characterization of conducting polymers is made difficult by their general insolubility in organic solvents. For example, the effects on the conductivity of poly(*p*-phenylene) of chain length and annealing and the presence of polynuclear structures and halogenation of end rings are not well understood.[17-26] How these affect the degree of crystallinity is also not known, and techniques that can address these questions are needed.

We report here solid-state deuterium NMR spectra of two conducting polymers in the undoped state. The first is poly(*p*-phenylene), and the second is predominantly *trans*-polyacetylene, prepared as a 13% blend with polystyrene. This paper demonstrates that solid-state deuterium NMR spectroscopy is particularly useful for (1) assessing the degree of crystallinity in these materials and (2) for determining the nature of molecular motion in the amorphous regions of these materials.

We and others have shown previously that solid-state deuterium NMR spectroscopy is a powerful tool for characterizing molecular motion in polymers.[27-30] In certain cases, molecular motion can be used as a criterion of crystallinity in polymers.[31] In particular, the ability of a phenyl ring to undergo 180° ring flips is a sensitive reporter of the conformational space, and thereby the degree of crystalline packing, in the vicinity of the aromatic ring.[31]

Because the theory of solid-state deuterium NMR spectroscopy and its application to polymers have been the subjects of recent reviews,[27-30] this background information will not be repeated here. Instead, we will briefly define two of the parameters of the solid-state deuterium NMR experiment that are useful for the characterization of these polymer samples. The first of these is the line shape, and the second is the relaxation time.[32] Both of these parameters have their origins in the fact that the deuterium nucleus is quadrupolar and has a nonspherical charge distribution around the nucleus. The NMR parameters are determined by the quadrupole interaction with the electric field gradient at the nucleus. It is the electric field gradient tensor that is averaged by molecular motion. Fluctuating electric field gradients produce relaxation, and large-amplitude motions average the deuterium line shape.

In particular, the static Pake line shape[33] is observed in powders in the absence of motion because of the orientation dependence of the resonance frequencies of the individual C–D bond vectors with respect to the external magnetic field. The total width of this static pattern is approximately 250 kHz. The static Pake pattern is averaged in highly specific ways when motions occur that have correlation times comparable to or less than the inverse of this line width.[27] The line shape can therefore be used to determine the amplitude and the frequency of large-amplitude molecular-level motions.

Although the deuterium NMR line shape provides information about the angular range of motion, it contains no further information about the rate of motion when these processes are fast on the time scale relevant to the line shape. Information about these faster motions can be

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obtained from deuterium NMR relaxation experiments, most notably from T_1 measurements.[34] Taken together, deuterium NMR line shapes and relaxation experiments can provide a fairly detailed analysis of the rate and angular range of molecular motions in polymers.

There have been a number of high-resolution solid-state ^{13}C NMR studies on both poly(*p*-phenylene)[35,36] and on polyacetylene[37-40], directed primarily at establishing the structures of these materials. In addition, the principal values of the ^{13}C chemical shift tensor have been determined for both *cis*- and *trans*-polyacetylene.[41] Solid-state proton NMR spectroscopy, whose relaxation in these polymers is dominated by the electronic spins, has been used to establish the details of electron spin diffusion along the chains in both doped and undoped polyacetylene.[42-45] Similar investigations have been performed by ESR[46,47] and by DNP (dynamic nuclear polarization).[44,47] In addition, solid-state deuterium NMR spectroscopy has been used to investigate polyacetylene[43,48] that was prepared according to the method of Shirakawa.[49] It is the purpose of this report to present new methods to evaluate the crystallinity in both poly(*p*-phenylene) and polyacetylene and to compare the previous deuterium NMR results on the Shirakawa material[43,48] with polyacetylene that has been prepared as a 13% blend in polystyrene.[50,51]

Materials and Methods

Samples. Poly(*p*-phenylene) was synthesized from perdeuteriobenzene with an $AlCl_3/CuCl_2$ catalyst–oxidant system[18] according to literature methods.[19-21] The material is light brownish yellow and is stable in air at temperatures in excess of 350 °C.

Laser desorption/Fourier transform mass spectra of the sample deposited on a stainless steel probe were recorded with a Nicolet FTMS-1000 spectrometer equipped with a Nicolet laser desorption interface and a Tachisto Tac-II pulsed CO_2 laser. These spectra demonstrated the presence of two major populations of oligomers, one having the expected structure for poly(*p*-phenylene) and the other exhibiting characteristics attributed to polynuclear structures.[23] Mass spectral analysis showed that most of the polymer was present as hexamers through dodecamers, centered at octamers. In addition, chlorinated oligomers are present in small amounts.[23] Approximately 60 mg of this sample was used for solid-state deuterium NMR analysis.

The polyacetylene sample was prepared as a 13% blend in polystyrene with a $Ti(OBu)_4/Et_3Al$ Ziegler-Natta catalyst at 85 °C according to literature methods.[50,51] Deuterated acetylene gas was used in the synthesis. When doped with iodine the conductivity is 5.3 S cm^{-1}. It has been shown that these blends of polyacetylene reach the percolation threshold at approximately 1% polyacetylene.[52] The undoped sample was placed in a dried tube (5 × 15 mm o.d.) in an inert atmosphere, capped with a plastic 5-mm NMR tube cap, and sealed with epoxy. This sample is predominantly the trans isomer and is black. A total of 105 mg of the blend was used for the analysis.

Solid-State Deuterium NMR Analysis. Solid-state deuterium NMR spectra were obtained on a home-built spectrometer operating at 55.26 MHz for deuterium. The spectrometer and its temperature control system have been described previously.[31,53] The probe employs a solenoid coil placed at right angles to the main field. The coil accepts samples that are 5 × 15 mm in size, and the probe has a 90° pulse width of 3.0 μs. Spectra were acquired in quadrature by using a total of 4096 points and a digitization rate of 100 ns per point (10 MHz). A number of variations on the quadrupole echo pulse sequence[54-56] were used to acquire the data (see below). In all cases, the delays between the echo pulses (t_1 and t_2) were 30 and 33 μs, respectively. Acquisition was set to begin just prior to the echo maximum, and the resulting free induction decays were shifted left so that the part of the free induction decay that was Fourier transformed began at the exact top of the echo maximum.

The pulse sequences used in this study have been described previously[31] and will only be briefly outlined here. The *quadrupole echo pulse sequence*[54-56] $(90_{\pm x} - t_1 - 90_y - t_2 - \text{acquire} - T)$ was used with varied repetition rates (T) to obtain the progressive saturation data and to acquire the fully relaxed spectra. The *amorphous quadrupole echo pulse sequence*[31] $((90 - 2\ \text{ms})_5 - t_a - 90_{\pm x} - t_1 - 90_y - t_2 - \text{acquire} - T)$ provides selective observation of components that have short T_1 values. the optimum time for t_a is approximately 3 times the T_1 of the amorphous regions. Inversion–recovery T_1 measurements of the amorphous components were obtained by using the *amorphous inversion–recovery quadrupole echo pulse sequence*.[31] This sequence is $(90 - 2\ \text{ms})_5 - t_a - 180 - \tau - 90_{\pm x} - t_1 - 90_y - t_2 - \text{acquire} - T)$, where τ is the variable delay time.

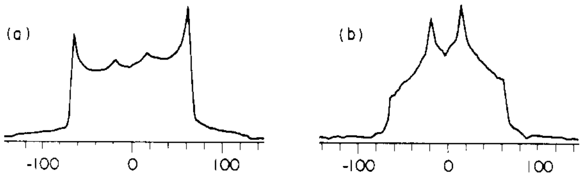

Figure 1. Solid-state deuterium NMR spectra of poly(*p*-phenylene) obtained at 23 °C and 55.26 MHz. The spectrum in a was obtained with the standard quadrupole echo pulse sequence, using a 60-s recycle delay time. The spectrum in b was obtained with the amorphous quadrupole echo pulse sequence, using a t_a delay of 100 ms.

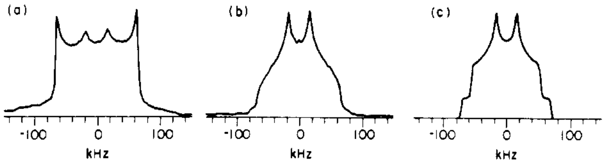

Figure 2. Solid-state deuterium NMR spetra for poly(*p*-phenylene) obtained at 50 °C and 55.26 MHz. The spectrum in a is the fully relaxed quadrupole echo spectrum obtained with a 60-s recycle delay. The spectrum in b represents the amorphous component and was obtained with the amorphous quadrupole echo pulse sequence, using a t_a delay of 100 ms. The spectrum in c is a computer simulation assuming rapid ($\tau_c < 10^{-7}$ s) 180° flips of the phenyl rings.

Spin–lattice relaxation times were determined either from the peak heights or from the areas of the line shapes. Equivalent results were obtained for both cases. The peak height was taken as the most intense singularity in the powder pattern. The T_1 plots are not strictly linear, and the reported T_1 values are estimates, taken from the early parts of the decay curves.

Solid-state deuterium NMR spectra were calculated according to the methods described by Mehring.[57] The calculations have been corrected for pulse power falloff as a function of frequency.[58]

Results and Discussion

Poly(*p*-phenylene). 1. General Description of Spectra. Solid-state deuterium NMR spectra of poly(*p*-phenylene) are shown in Figure 1. When observed under equilibrium conditions (i.e., with a recycle delay, T, that is long enough to represent accurately the signals from both the crystalline and amorphous components), the spectrum shows predominantly a static pattern (Figure 1a), where the quadrupole splitting, $\Delta\nu_q$, is approximately 130 kHz. However, there are two distinct singularities toward the center of this pattern, separated by approximately 32 kHz. That these central components arise from phenyl rings that are undergoing rapid ($\tau_c < 10^{-7}$ s) 180° flips can be seen from the adjacent amorphous quadrupole echo spectra (Figure 1b).

The effects of increased temperature are shown by the spectra in Figure 2, taken at 50 °C. Although this modest increase in temperature of 25 °C does not drastically change the overall appearance of the spectrum (Figure 2a), it is clear from Figure 2b that all of the rings which are flipping are now doing so rapidly compared to the spectrometer time scale. At 50 °C, the spectrum for the flipping rings (Figure 2b) fits very well to a theoretically

Table I
Percent of Poly(*p*-phenylene) Undergoing Rapid Ring Flips[a]

23 °C	50 °C
21	28

[a] Uncertainty = ±5%.

calculated spectrum (Figure 2c).

We have established in other polymers that whether or not a phenyl ring is able to undergo a 180° flip is a good indicator of the conformational space surrounding the ring[31,59] and that the presence of phenyl ring flips can be associated with amorphous regions of polymers.[31] By subtracting the data in Figure 1b from the data in Figure 1a, one can estimate the crystalline fraction of the poly(*p*-phenylene) sample. The same procedure can be performed for the data in Figure 2. These results are summarized in Table I, where it is seen that the sample is approximately 75% crystalline (i.e., 25% amorphous). It is also evident from these data that the apparent degree of crystallinity decreases slightly as the temperature is raised.

Thermal disorder measured by X-ray crystallography for the linear model compounds biphenyl,[60] *p*-terphenyl,[61] quaterphenyl,[62] and poly(*p*-phenylene)[63,64] tends to support the conclusions drawn from the present solid-state deuterium NMR results. The mean squared librational amplitudes, $\langle \phi^2 \rangle$, for the rings in these molecules, are $106^{\circ 2}$, $70^{\circ 2}$, and $72^{\circ 2}$, respectively. It is evident that there is ample precedent for the occurrence of phenyl librations over angles of approximately ±10° in para-substituted phenylene oligomers. It has been shown that similar librations occur in the crystalline regions of poly(*p*-phenylene),[65] and that they serve to shorten the relaxation times for the protons in the crystalline regions.[66]

The 180° phenyl ring flips observed in the amorphous regions may serve to explain in part the anomalous ^{13}C NMR intensities previously reported for the protonated carbons in the ^{13}C cross-polarization, magic angle spinning NMR spectrum of poly(*p*-phenylene).[35,66] It is likely that a fraction of the rings are flipping at frequencies that would set up strong local fluctuating dipolar fields. These fields would produce a broadening that could not be removed by high-power proton decoupling.[67,68] The extent of broadening observed would be particularly sensitive to the strength of the decoupling field. Such phenomena have been reported for other polymers, most notably poly(ethylene oxide).[68]

There is compelling evidence from mass spectroscopy and other sources which suggests that some nonideal transformations occur with metal halide catalyst–oxidant systems that catalyze polymerization.[23,25,26] The sample of deuterated poly(*p*-phenylene) used for the experiments reported here contains some polynuclear oligomers. The fused polynuclear ring moiety is not expected to exhibit large amplitude ring motions and thus will not contribute to the narrowed line shapes of the polynuclear aromatic model compound. That this is true was confirmed experimentally by solid-state deuterium NMR experiments on triphenylene-d_{12}. The spectra of this compound (not shown) provide no evidence of rapid ring motions and furthermore show that this material has an exceptionally long deuterium spin–lattice relaxation time.

2. Relaxation Experiments. The relaxation times of both the static and the mobile fractions of poly(*p*-phenylene) were estimated from progressive saturation and inversion–recovery measurements, respectively. Figure 3 shows representative progressive saturation data for poly(*p*-phenylene). The static component is dominant in the spectra obtained at long delay times. As the delay becomes shorter and shorter, the pattern from the rapidly flipping phenyl rings contributes an increasingly larger fraction of signal intensity, causing some error in these measurements. Representative plots of the progressive saturation data are shown in Figure 4, and the spin–lattice relaxation time of the static component is listed in Table II. It is significant to note that the relaxation time for the crystalline component of poly(*p*-phenylene) is significantly shorter than that of the polyacetylene blend (see Table II and discussion, below). It is likely that considerable low amplitude librational motion exists in the crystalline regions of poly(*p*-phenylene).[60–62,69] These motions would not affect the line shape to an appreciable

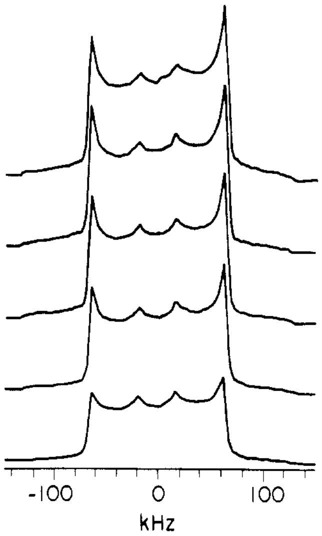

Figure 3. Representative progressive saturation solid-state deuterium NMR spectra of poly(*p*-phenylene) obtained at 23 °C and 55.26 MHz. From top to bottom, the recycle delay times were 60, 30, 10, 5, and 2 s.

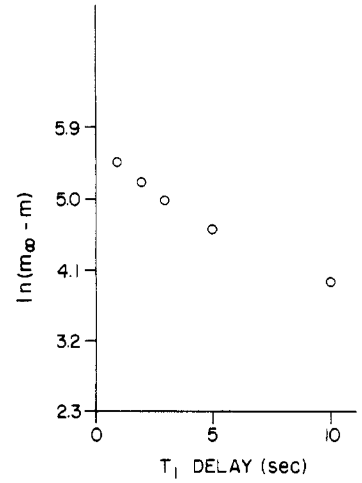

Figure 4. Representative progressive saturation data for poly(*p*-phenylene) obtained at 23 °C and 55.26 MHz.

Table II
Spin–Lattice Relaxation Times (s)[a]

	23 °C	50 °C
Crystalline Component		
poly(*p*-phenylene)	6.1	5.5
polyacetylene	10.5	7.2
Amorphous Component		
poly(*p*-phenylene)	0.029	0.025

[a] Uncertainty = ±20%.

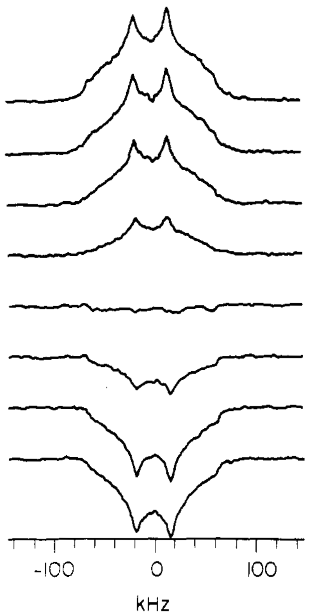

Figure 5. Solid-state deuterium NMR inversion recovery data for the amorphous component of poly(*p*-phenylene). The data were obtained at 50 °C and 55.26 MHz by using the amorphous quadrupole echo inversion—recovery pulse sequence with an amorphous delay, t_a, of 100 ms and a train of five presaturating 90° pulses separated by 2 ms.

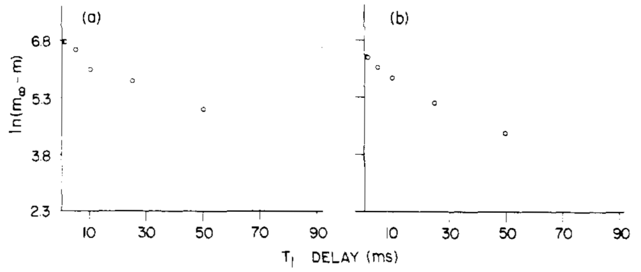

Figure 6. Plots of the inversion–recovery T_1 data for poly(*p*-phenylene) obtained at 23 (a) and 50 °C (b).

extent but would contribute to a shortened spin–lattice relaxation time.

The amorphous inversion–recovery quadrupole echo pulse sequence was used to selectively measure the spin–lattice relaxation times of the rapidly flipping phenyl rings in poly(*p*-phenylene). Representative data are shown in Figure 5. These spectra show no appreciable anisotropy in relaxation across the line shape, as would be expected for a precise two-site hop with a single correlation time.[34] Washing-out of this anisotropy is taken as evidence for a distribution of motional correlation times. It furthermore shows that additional low-amplitude motions may be superimposed on the 180° ring flips.[31,70] The data points for the inversion–recovery experiment are shown in Figure 6. These are not strictly linear, again suggesting that the motion of the phenyl rings is characterized by a distribution of correlation times. The results are summarized in Table II. The data show only a slight change with temperature, suggesting that the T_1 is near its minimum and that the minimum is shallow. A correlation time of 1×10^{-7} s can be estimated for the amorphous rings by combining the T_1 data with the equations of Torchia and Szabo.[34] This estimate is in good agreement with the implications from the line shapes.

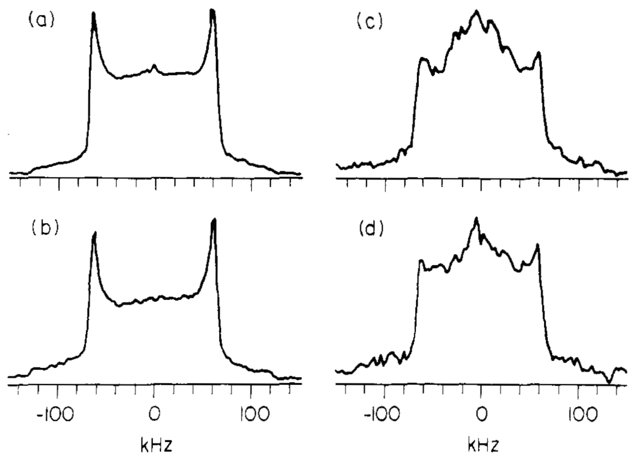

Figure 7. Solid-state deuterium NMR spectra of polyacetylene as a 13% blend in polystyrene, obtained at 23 (top row) and 50 °C (bottom row) and at 55.26 MHz. The left column represents equilibrium spectra that were obtained with a 60-s recycle delay. The spectra in the right column were obtained with the amorphous quadrupole echo pulse sequence, using a 300-ms delay for t_a.

Polyacetylene as a Blend in Polystyrene. 1. General Description of Spectra. Fully relaxed solid-state deuterium NMR spectra of polyacetylene as a blend in polystyrene are shown in the left column of Figure 7 at 23 (top) and 50 °C (bottom). These data show that the spectrum is dominated by a static component with a quadrupolar splitting of approximately 128 kHz. Other workers have measured the same quadrupolar splitting for polyacetylene prepared by the Shirakawa method.[43] The center of the spectrum in Figure 7a shows evidence of an additional, more mobile component. This component can be selectively observed by using the amorphous quadrupole echo pulse sequence, as shown in Figure 7c. The spectrum of Figure 7c is somewhat reminiscent of the solid-state deuterium NMR spectrum of the amorphous component of polyethylene, in which there exist many competing types of motions.[71] It is interesting to note that the contribution of this amorphous component appears to decrease as the temperature is increased (cf. parts a and b of Figure 7). This is consistent with the presence of considerable molecular motion during the quadrupole echo delay time. Because this motion produces homogeneous broadening, this part of the line shape is not refocused properly, and its intensity drops out of the spectrum.

The fraction of crystallinity can be estimated as 80% from these spectra. Shirakawa polyacetylene of the trans conformation has been reported to have a similar fraction of crystallinity.[43]

2. Relaxation Experiments. Representative progressive saturation solid-state deuterium NMR data are shown in Figure 8 for the polyacetylene blend in polystyrene. The static-like singularities of the spectrum persist even at short delay times. The T_1 for the static component is estimated to be 10.5 s (Table II). This time is somewhat longer than the 6.5 s that has been reported for the Shirakawa polymer.[43] Because the present relaxation time was measured from a series of spectra, rather than from a single decay, it is likely that this new value more closely represents the relaxation time for both materials. The relaxation time for the amorphous component is estimated to be approximately 1 s. It is clear from inversion–recovery spectra at delay times covering several orders of magnitude that motions in the amorphous regions of this material are characterized by a broad distribution of characteristic frequencies.

Summary

Poly(*p*-phenylene). These solid-state deuterium NMR results demonstrate that approximately 25% of the phenyl rings in poly(*p*-phenylene) is involved in 180° flips about the 1,4-phenylene axis. A combination of relaxation ex-

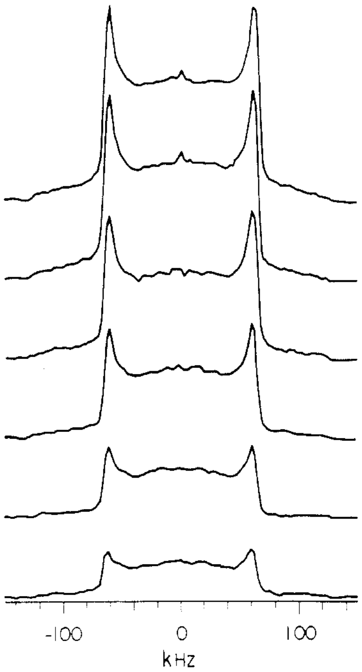

Figure 8. Representative progressive saturation solid-state deuterium NMR spectra of polyacetylene as a 13% blend in polystyrene. The data were obtained at 23 °C and 55.26 MHz, using delay times of 60, 30, 10, 5, 2, and 1 s (from top to bottom).

periments and line shape analyses shows that the correlation time for the flipping process, τ_c, is approximately 1×10^{-7} s at 23 °C. These flipping rings are associated with the amorphous regions of the material.

The relaxation times for the static rings are shorter than would be expected for a rigid crystalline material. It is likely that there are additional high-frequency, low-amplitude librational motions that produce relaxation. Comparison with model compounds bears this out.

Polyacetylene as a Blend in Polystyrene. The polyacetylene examined in this study differs from the normal Shirakawa polymer in that the present material was prepared as a 13% blend in polystyrene. This method of preparation raises questions concerning the local morphology of the acetylene polymer. The solid-state deuterium NMR results reported here indicate that the polyacetylene blend and the conventional Shirakawa material are very similar from a spectroscopic point of view. Because both materials have approximately the same degree of crystallinity, it is likely that the polyacetylene is not distributed homogeneously in the polystyrene matrix. Recent neutron diffraction measurements support this finding.[72]

The solid-state deuterium NMR results show that approximately 20% of the polyacetylene in the blend is in amorphous regions in which very complex molecular motions occur. The line shapes for the amorphous material are similar to those observed for the amorphous regions of polyethylene, in which 3-bond, 5-bond, 10-bond, and longer range motions, all occurring with a distribution of motional correlation times, produce very complex line shapes.[71]

Taken together, these results show the technique of solid-state deuterium NMR spectroscopy holds much promise for the characterization of crystallinity and morphology in these and other intractable materials.

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Registry No. Poly(*p*-phenylene), 25190-62-9; polyacetylene, 25768-71-2; polystyrene, 9003-53-6.

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Analysis of the Surface Structure of a Built-Up Film of Fluorocarbon Amphiphile and Polymer/(Fluorocarbon Amphiphile) Composite Thin Film by Means of X-ray Photoelectron Spectroscopy

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ABSTRACT: Angular dependent X-ray photoelectron spectra were obtained for the Langmuir–Blodgett (LB or built-up) film of a fluorocarbon amphiphile with two fluoroalkyl chains and a poly(vinyl alcohol)/(fluorocarbon amphiphile) composite thin film. A simple layer model was proposed to estimate the photoelectron mean free path in fluorocarbon bilayers. A comparison of the angular dependences of the observed XPS intensity with the calculated intensity for built-up film revealed that the photoelectron mean free path for C_{1s} photoelectron (kinetic energy of ca. 970 eV) in built-up film is ca. 4.0 nm. Fluorocarbon amphiphilic molecules in the composite thin film form highly oriented bilayer lamella. The surface enrichment of fluorocarbon amphiphile in the surface of the composite thin film facing the air was confirmed by X-ray photoelectron spectroscopy. Application of layer models to the calculation of the composition profile of the composite thin film revealed that the surface of the composite thin film which contains more than 19 wt % amphiphile was completely covered with an oriented bilayer of the amphiphile.

Introduction

The structure and properties of Langmuir–Blodgett (LB or built-up) films have received much attention recently. This is due to the fact that the control of the state of molecular aggregation is easily achieved by the preparation technique developed by Langmuir[1] and Blodgett.[2] Application studies concerning electron conduction, semiconductors, biomaterials, etc. have been carried out by several authors.[3-5]

X-ray photoelectron spectroscopy is a useful technique to characterize the surface composition of solids. Estimation of the photoelectron mean free path in organic solids has been achieved by utilizing built-up films.[6-8] Since the built-up film forms a highly ordered layer structure, it is a suitable material for the estimation of the photoelectron mean free path. The electron mean free path of the C_{1s} photoelectron (kinetic energy of ca. 970 eV) in the built-up films of long-chain fatty acids ranges from 4 to 5 nm.[8]

A series of amphiphiles containing fluoroalkyl chains have been synthesized by Kunitake and co-workers.[9,10] Fluorocarbon amphiphiles form a bilayer structure in water and show phase transition behavior similar to that observed for biological lipids or artificial hydrocarbon amphiphiles.[11-13] The fluorocarbon amphiphiles can be immobilized by casting an aqueous solution of amphiphile with aqueous poly(vinyl alcohol).[14] The fluorocarbon amphiphile molecules in this composite thin film form highly

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